

Advances in **ORGANOMETALLIC CHEMISTRY**

EDITED BY

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I

INTRODUCTION

Although nuclear magnetic resonance (NMR) is a relatively new spectroscopic technique, it has already found wide application in the solution of chemical problems, including numerous applications to the study of organometallic compounds. Chemical shift and spin-spin coupling data enable the chemist to determine the location of magnetically active nuclei in a molecule of interest, and to obtain preliminary structural information often not as readily deducible by other methods of spectroscopy.

In addition, because of the quantum mechanical time scale of the NMR experiment, one can study certain time-dependent phenomena which are not generally accessible to the other branches of spectroscopy. Both molecular motion and chemical exchange may affect the appearance of NMR spectra. This unique characteristic is finding significant application in the study of organometallic compounds. The present review is designed to

provide information of benefit to the organometallic chemist who uses NMR as an investigative tool. We have assumed that the reader has a basic understanding of the theory and practice of NMR spectroscopy. Those who do not may find it helpful to consult one of several excellent texts and reviews now available on NMR spectroscopy (2, 155, 174, 257, 289, 290, 300, 301, and 339).

We have chosen to define the term "organometallic" as referring to compounds which contain carbon atoms directly bonded to metal atoms. Principally because of restriction of space, we have not attempted to treat comprehensively the derivatives of the metalloid elements boron, silicon, and phosphorus. However, we have included selected compounds of these elements where these would supplement the discussions of other organometallic derivatives. Although we have attempted to present a comprehensive coverage of all the data available, the rapid growth of this field may have caused some inadvertent omissions.

II

CHEMICAL SHIFT AND SPIN-SPIN COUPLING

A. Theory

1. Chemical Shifts

The calculation of chemical shifts is closely related to the calculation of diamagnetic susceptibilities, which has been a long-standing problem to chemists in general. The attempts thus far have made use of valence-bond or other molecular wave functions and even for simple molecules are necessarily approximate. Developments in this general area have recently been reviewed (see, for example, Meiboom, 248a), but very few papers have been concerned directly with organometallic systems. The difficulty of matching calculated to observed values is that the experimental data are extremely precise—relative differences in most proton chemical shifts for instance are measured in parts per million—while our quantitative knowledge of the electron distribution in molecules simply has not come down to such precision. However, the chemical shifts of protons bound directly to transition metals show a much larger variation than do those bonded to carbon (25, 56, 57, 59, 141, 153, 374), and are somewhat more amenable to calculation. These have been carried out by Stevens, Kern, and Lipscomb (347a) for HCo(CO)_4 and by Lohr and Lipscomb (219) for a series of related compounds, using a modification of the

Ramsey theory [cf. (209), Ch. 7] developed by Kern and Lipscomb (188a) to eliminate the need for a knowledge of excited states. More recently, Buckingham and Stephens (42a) have shown that this treatment is inadequate in complexes where the paramagnetic shielding σ^p contributes substantially to the total shielding.

Several organometallic compounds were included in a study of the effect of electronegativity and magnetic anisotropy of substituents on C^{13} and H^1 chemical shifts in CH_3X and CH_3CH_2X , by Spiesecke and Schneider (344). This work was an extension on and improvement of earlier work (10).

Pitcher, Buckingham, and Stone (285) have discussed the anomalous chemical shift of fluorine atoms bonded to the α -carbon atom of perfluoroalkyl-transition metal derivatives in terms of mixing of nonbonding electrons of the halogen with orbitals of the metal. Bennett, Pratt, and Wilkinson (27) have discussed the shielding of protons of olefins in the complexes of these ligands with transition metals.

2. Spin-Spin Coupling Constants

A calculation of spin-spin coupling constants using the valence-bond approximation was carried out by Klose (211) for alkyl derivatives of Si, P, Se, Cd, Sn, Te, Hg, Tl, and Pb. The agreement with observed values was gratifying in most cases, which included opposite signs for CH_3-M and $-CH_2-M$ (see discussion of observed spectra for ethyl derivatives, below). The effect of substituents on coupling constants for $Si^{29}-H$ (and $C^{13}-H$) has been studied by Juan and Gutowsky (181a). They find that the effect of substituent on the s character in the bonding orbital of the central atom and the contact term are the dominant mechanisms responsible for the magnitude of the coupling.

Correlation of coupling constants with atomic number in series of derivatives (including some organometallic compounds) in which hybridization parameters are equal or comparable has been carried out by Reeves and Wells (298)¹.

B. Experimental Observations

1. General Comments

Experimental data are summarized in the sections below. Certain empirical relations between the data should become apparent from these Tables.

¹ For later papers in this vein see Inglefield and Reeves [(178a), and references cited therein; Smith (342); and Tzalmuna (358a)].

These have often been noted by investigators, and are presented in the discussion below. In other instances they await recognition by readers of this article. In view of the limitations of present theoretical treatments, such empirical relations are important. First, they allow one to assess important structural features of the molecules under study from the data available. In addition, these relations may serve as a guide for future theoretical developments.

Methods for determining magnetic susceptibility by magnetic resonance have been reported and these should be of general interest (105*a*, 129*b*, 133*a*).

In order to facilitate the comparison of NMR data reported relative to a variety of standards, an attempt has been made in the Tables to convert all values to a common reference scale. For protons, the τ scale (cf. Tiers, 353) has been used. On this scale, $(\text{CH}_3)_4\text{Si}$ is the reference compound and is assigned the value $\tau = 10$. Data for which a different scale was used are listed in the Tables as originally reported, together with the approximate equivalent τ value, obtained according to the conversion factors given below. Similarly, F^{19} chemical shifts have been standardized relative to CCl_3F . The conversions must be considered only approximate, being accurate to ± 0.1 to 0.3 ppm. We have followed the sign convention that positive values increase to higher field. In some instances, this has required inversion of the signs used in the original report.

CONVERSION FACTORS FOR CHEMICAL SHIFTS^a

$$\tau = \delta_{(\text{CH}_3)_4\text{Si}} = \begin{cases} \delta_{\text{H}_2\text{O}} + 5.22 \\ \delta_{\text{C}_6\text{H}_{11}} + 8.57 \\ \delta_{\text{CHCl}_3} + 2.65 \\ \delta_{\text{C}_6\text{H}_6} + 2.63 \\ \delta_{\text{CH}_2\text{Cl}_2} + 4.70 \end{cases} \quad \phi = \delta_{\text{CCl}_3\text{F}} = \begin{cases} \delta_{\text{CF}_3\text{COOH}} + 76.6 \\ \delta_{\text{C}_6\text{F}_6} + 132.1 \\ \delta_{\text{C}_6\text{H}_5\text{CF}_3} + 63.6 \\ \delta_{\text{C}_6\text{F}_6} + 163.7 \end{cases}$$

^a See (37); for protons see also, "Varian Catalogue," No. 1, Varian Assoc., Palo Alto, Calif.; and for F^{19} , see (31*a*), (112), and (257*b*).

Compounds containing more than one kind of ligand are cross-referenced in the appropriate Tables.

2. σ -Bonded Derivatives

Chemical shifts and spin-spin coupling data for σ -bonded organometallic compounds are summarized in Tables I through IX. Within each table, the

compounds are arranged in the order of the groups in the Periodic Table, with derivatives of the main group elements preceding those of the transition metals. When more than one set of data is available for a given compound, each set has been listed separately.

Chemical shift and coupling data not directly involved with the organic group under consideration have been included in the Tables under "Remarks."

Methyl Derivatives (Table I). Due to the simplicity of the spectra of methyl derivatives of the metals, they have been favored for studies of various electronic effects of the metal atom, and data are therefore available for a large number of these compounds.

There has been considerable speculation over a long period of time concerning the structure of dialkylaluminum chlorides and alkylaluminum dichlorides. These compounds, as well as the trialkylaluminums, are dimeric in solution. In order for $(\text{CH}_3)_6\text{Al}_2$, for instance, to exist as a dimer, bridging methyl groups must be invoked. On the other hand, in the case of the alkylaluminum chlorides, bridging could occur alternatively *via* the chlorine atoms, and for various reasons this has often been held to be more probable. Several groups of investigators (154, 175, 260) have succeeded in demonstrating that at low temperatures $(\text{CH}_3)_6\text{Al}_2$ does indeed exhibit two distinct resonances, and that the proton resonance of $(\text{CH}_3)_4\text{Al}_2\text{Cl}_2$ gives no indication of dividing or even broadening at temperatures down to about -75° . It has thus been concluded that the alkylaluminum chlorides bridge through chlorine atoms.

Numerous studies have been made on methyl derivatives of the Group IV elements. Allred and Rochow (11) have suggested a correlation between chemical shifts of $(\text{CH}_3)_4\text{M}$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) and the electronegativities of the central atoms. On the basis of this and other evidence they have concluded that there is an alternation in electronegativities as one descends the elements of the fourth group. Kaesz and Holmes (176) have observed the proton resonances of solutions of the methyltin chlorides and have suggested a correlation between the changes in $\text{Sn}-\text{H}$ spin-spin coupling constants and the hybridization of the tin orbitals in the various methyltin cations assumed to be present.

Several studies of methyl derivatives of the Group IV elements have involved estimations of the extent to which the d orbitals of these atoms, especially silicon, are engaged in $d_\pi-p_\pi$ overlap with substituent groups. For instance, Brown and Webster (34) have studied the series of compounds

TABLE I
METHYL DERIVATIVES

Compound	δ (ppm)	τ (ppm)	Rel- ative inten- sity	\mathcal{J} (cps)	Remarks	References
<i>Group I</i>						
MeLi	—	11.3	—	—	5% in ether	128
<i>Group II</i>						
MeMgI	—	11.3	—	—	5% in ether	128
Me ₂ Mg	—	11.3	—	—	1% in ether	128
<i>Group III</i>						
Me ₃ B	—	9.21	—	—	$\delta_{\text{BF}_3-\text{OEt}_2} = -85$	140
Me ₃ B	4.57 (CH ₂ Cl ₂)	9.2	—	—		73
Me ₃ B	—	—	—	—	$\delta_{(\text{MeO})_2\text{B}^{11}} = -68.2$	282
Me ₃ B:NMe ₃	5.65 (CH ₂ Cl ₂)	10.3	—	—	$\tau_{\text{Me}_3\text{N}} = 2.93$	73
Me ₂ BVi	—	9.18	—	—	$\tau_{\text{VI}} = 3.65$, $\delta_{\text{BF}_3-\text{OEt}_2} = -74.5$	140
MeBF ₃ /H ₂ O	—	—	—	—	$\delta_{\text{CCl}_4\text{F}} = 132$, $\mathcal{J}_{\text{B}^{11}-\text{F}} = 64$	346
MeBVi ₂	—	9.14	—	—	$\tau_{\text{VI}} = 3.52$, $\delta_{\text{BF}_3-\text{OEt}_2} = -64.4$	140
(Me ₃ Al) ₂	1.82 (C ₅ H ₁₀)	10.4	—	—	At -75° , $\tau = 9.7$, 10.8	154
(Me ₃ Al) ₂	—	10.29	—	—	22°C ; at -67° , $\tau = 9.69$, 10.59	175
(Me ₃ Al) ₂	1.75 (C ₆ H ₁₂)	10.3	—	—		39
(Me ₃ Al) ₂	1.79 (C ₅ H ₁₀)	10.4	—	—	Room temp.	260
(Me ₃ Al) ₂	1.04, 2.17 (C ₅ H ₁₀)	9.6, 10.7	—	—	-75°C , ratio 1:2	260
(Me ₂ AlCl) ₂	1.85 (C ₅ H ₁₀)	10.4	—	—	No splitting at -75°	154
(Me ₂ AlCl) ₂	—	10.32	—	—		175
(Me ₂ AlCl) ₂	1.75 (C ₅ H ₁₀)	10.3	—	—		39
(Me ₂ AlH) ₂	—	10.49	—	—		175

(Me ₂ AlOMe) ₂	—	10.79	—	—	175
(Me ₂ AlOEt) ₂	—	10.77	—	—	175
[Me ₂ AlOC(Me) ₃] ₂	—	10.54	—	—	175
(MeAlCl ₂) ₂	1.61 (C ₅ H ₁₀)	10.2	—	—	154
(MeAlCl ₂) ₂	1.45 (C ₆ H ₁₂)	10.0	—	—	39
(Me ₂ AlOSiMe ₃) ₂	Me-Al	10.82	2	—	319
	Me-Si	9.80	3	—	318
Me ₃ Al(Me ₂ NNMe ₂)	—	10.51	—	—	109
Me ₃ Al(Me ₂ NCH ₂ NMe ₂)	—	10.93	—	—	109
Me ₂ AlH : NMe ₃	2.295 (C ₆ H ₁₂)	10.86	3	—	281
MeAlH ₂ : NMe ₃	2.29 (C ₆ H ₁₂)	10.85	6	—	281
Me ₃ Al/NMe ₃	—	—	—	—	251
Me ₃ Al/NMe ₃	—	—	—	—	251
Me ₃ Al : NEt ₃	—	10.90	—	—	175
Me ₃ Al : NEt ₃	—	—	—	—	251
Me ₃ Al/NEt ₃	—	—	—	—	251
				τ _{CH₃} = 7.64, τ _{CH₂CH₃} = 9.22	
				2:5 ratio, τ _{CH₃} = 7.57, τ _{CH₂CH₃} = 9.08	
Me ₃ In	1.56 (C ₅ H ₁₀)	—	—	—	259
				Temp. dependent	
Me ₃ Tl	—	9.48	—	251	—85°
Me ₂ TlEt	—	9.58	—	223	—85° See Table II for ethyl group
MeTlEt ₂	—	9.73	—	187	—85° See Table II for ethyl group
Me ₃ Tl/Me ₂ O	—	—	—	269.6	—64°
Me ₃ Tl/Me ₃ N	—	—	—	270.3	—64°
Me ₃ Tl	—	—	—	250.4	—50° in PhCD ₃
Me ₂ TlVi/Me ₂ O	—	—	—	294.6	See Table V for Vi group
Me ₂ TlVi/Me ₃ N	—	—	—	295.5	See Table V for Vi group
MeTlVi ₂ /Me ₂ O	—	—	—	316.8	
MeTlVi/Me ₃ N	—	—	—	317.4	
Me ₂ TlI	—0.345 (C ₆ H ₁₂)	8.22	—	413.4 ^a	Pyridine soln
Me ₂ TlClO ₄	—0.340 (C ₆ H ₁₂)	8.22	—	415.5 ^a	Pyridine soln
				406.0 ^a	D ₂ O soln

TABLE I—*continued*

Compound	δ (ppm)	τ (ppm)	Rel- ative inten- sity	γ (cps)	Remarks	References
Me ₂ TlOH	+0.09 (C ₆ H ₁₂)	8.65	—	421.0 ^a	Pyridine soln	159
				406.0 ^a	D ₂ O soln	159
(Me ₂ Tl) ₃ PO ₄	0.12 (C ₆ H ₁₂)	8.68	—	421.0 ^a	Pyridine soln	159
				406.0 ^a	D ₂ O soln	159
Me ₂ TlMnO ₄	0.10 (C ₆ H ₁₂)	8.66	—	421.5 ^a	Pyridine soln	159
				407.5 ^a	D ₂ O soln	159
(Me ₂ Tl) ₂ CO ₃	0.05 (C ₆ H ₁₂)	8.61	—	422.0 ^a	Pyridine soln	159
				407.0 ^a	D ₂ O soln	159
Me ₂ TlCN	−0.166 (C ₆ H ₁₂)	8.39	—	423.5 ^a	Pyridine soln	159
Me ₂ TlSCN	−018 (C ₆ H ₁₂)	8.38	—	426.5 ^a	Pyridine soln	159
				406.0 ^a	D ₂ O soln	159
Me ₂ Tl lactate	0.01 (C ₆ H ₁₂)	8.57	—	429.0 ^a	Pyridine soln	159
				408.0 ^a	D ₂ O soln	159
Me ₂ Tl trifluoroacetate	−0.11 (C ₆ H ₁₂)	8.45	—	432.0 ^a	Pyridine soln	159
				406.5 ^a	D ₂ O soln	159
Me ₂ TlF	—	—	—	407.0 ^a	D ₂ O soln	159
(Me ₂ Tl) ₂ SO ₄	—	—	—	408.0 ^a	D ₂ O soln	159
(Me ₂ Tl) ₂ CrO ₄	—	—	—	406.5 ^a	D ₂ O soln	159
<i>Group IV</i>						
Me ₄ Si	4.74 (H ₂ O)	10.00	—	—		11
Me ₄ Si	—	10.00	—	—		34
Me ₄ Si	8.0 cps (gaseous CH ₄)	—	—	—	Footnote b. $\delta_{C^{13},H_4} = 129.0$ ppm, $\gamma_{C^{13}-H} = 119$	344
Me ₄ Si	—	—	—	6.8		211

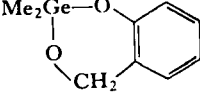
Me ₄ Si	—	—	—	—	$J_{C^{13}-H} = 119$	233
Me ₃ SiCl	—	9.58	—	—		34
Me ₃ SiCl	0.9 (C ₆ H ₁₂)	9.5	—	—		349
Me ₃ SiVi	—	8.62	—	—	See Table V for vinyl group	172
Me ₃ SiH	—	9.92	—	—	$\tau_{SiH} = 6.15$	366
Me ₂ SiVi ₂	—	8.68	—	—	See Table V for vinyl group	172
Me ₂ SiCl ₂	—	9.20	—	—		34
Me ₂ PhSiH	—	9.68	—	—	$\tau_{SiH} = 5.57$. See Table VII for Ph	366
Me ₂ ClSiH	—	9.49	—	—	$\tau_{SiH} = 5.13$	366
MeSiCl ₃	—	8.86	—	—		35
MeCl ₂ SiH	—	9.12	—	—	$\tau_{SiH} = 4.42$	366
MePh ₂ SiH	—	9.46	—	—	$\tau_{SiH} = 5.08$. See Table VII for Ph	366
Me ₆ Si ₂	—	9.96	—	—		34
Me ₆ Si ₂ O	—	9.95	—	—		34
Me ₄ Ge	—	9.873	—	2.92		341
Me ₄ Ge	4.62 (H ₂ O)	9.88	—	—	CCl ₄ soln	296
Me ₄ Ge	4.62 (H ₂ O)	9.88	—	—		11
Me ₄ Ge	—	9.87	—	—		362
Me ₄ Ge	0.0 cps (gaseous CH ₄)	—	—	—	$\delta_{C^{13}, H_4} = 130.4$ ppm. Footnote <i>b</i> . $J_{C^{13}-H} = 126$	344
Me ₄ Ge	—	—	—	—	$J_{C^{13}-H} = 124$	233
Me ₆ Ge ₂	—	9.79	—	—		35
Me ₆ Ge ₂ O	—	9.70	—	—		35
Me ₃ GeOLi	—	9.634	—	—		312
Me ₃ GeSeLi	—	9.37	—	—		313
[Me ₃ Ge] ₂ Se	—	9.34	—	—		313
	—	9.34	—	—	$\tau_{CH_2} = 5.3$, $\tau_{Ph} = 3.2$	373

TABLE I—continued

Compound	δ (ppm)	τ (ppm)	Rel- ative inten- sity	\mathcal{J} (cps)	Remarks	References
$\text{Me}_3\text{GeOSiMe}_3$	—	9.65	—	—	$\mathcal{J}_{\text{C}^{13}\text{H}} = 126.0, 117.8$; $\tau_{\text{SiMe}_3} = 10.00$; $\mathcal{J}_{\text{Si}^{19}\text{Me}} = 6.8$	319 318
$\text{Me}_3\text{GeOSiEt}_3$	—	9.59	—	—	$\tau_{\text{CH}_2} = 9.47$, $\mathcal{J}_{\text{HH}} = \approx 8.0$, $\tau_{\text{SiCH}_2\text{CH}_3} = 8.0$	319 318
$\text{Me}_2\text{Ge}(\text{OSiMe}_3)_2$	—	9.52	—	—	$\tau_{\text{SiMe}} = 9.94$	319
$\text{MeGe}(\text{OSiMe}_3)_3$	—	9.40	—	—	$\tau_{\text{SiMe}} = 9.92$	319
$\text{Me}_3\text{Ge}(\text{C}_3\text{H}_5) \text{ cis}$	—	9.75	—	—	See Table VI for C_3H_5	331
$\text{Me}_3\text{Ge}(\text{C}_3\text{H}_5) \text{ trans}$	—	9.82	—	—	See Table VI for C_3H_5	331
Me_4Sn	—	9.93	—	—		34
Me_4Sn	7.15 (C_6H_6)	9.78	—	—		55
Me_4Sn	—	9.93	—	51.1, 53.4		182
$\text{Me}_4\text{Sn}^{119}$	1.36 (C_6H_{12})	9.9	—	54.2	$\mathcal{J}_{\text{C}^{13}\text{-H}} = 127.0$	209
$\text{Me}_4\text{Sn}^{117}$	—	—	—	51.9		209
Me_4Sn	—	9.94	—	51.8, 54.1		35
Me_4Sn	4.70 (H_2O)	9.96	—	—		11
$\text{Me}_4\text{Sn}^{119}$	—	—	—	54		45
Me_4Sn	—	—	—	51.5, 54.0	31° C	176, 361
Me_4Sn	—	—	—	—	$\mathcal{J}_{\text{C}^{13}\text{-H}} = 128$	233
Me_4Sn	6.0 cps (gaseous CH_4)	—	—	—	$\delta_{\text{C}^{13}, \text{H}_4} = 137.6$ ppm. Footnote b. $\mathcal{J}_{\text{C}^{13}\text{-H}} = 128$	344
Me_3SnCl	6.65 (C_6H_6)	9.28	—	—		55
Me_3SnCl	—	9.37	—	—		34
$\text{Me}_3\text{Sn}^{117}\text{Cl}$	—	—	—	55.5		233

$\text{Me}_3\text{Sn}^{119}\text{Cl}$	—	—	—	58.5		233
Me_3SnCl	—	—	—	57.4, 59.7	40° C	176, 361
Me_3SnBr	6.60 (C_6H_6)	9.23	—	—		55
Me_3SnCF_3	6.98 (C_6H_6)	9.61	—	—	$\delta_{\text{CF}_3\text{CO}_2\text{H}} = -29.1$	55
Me_3SnH	—	9.82	—	54, 56	$\tau_{\text{SnH}} = 5.27$; $\mathcal{J}_{\text{HSnCH}} = 2.4$; $\mathcal{J}_{\text{SnH}} = 1744$, 1664; $\mathcal{J}_{\text{C}^{13}\text{H}} = 128.5$	127
$\text{Me}_3\text{Sn}^-\text{Li}^+/\text{MeNH}_2$	—	10.4	—	14		127
Me_2SnCl_2	6.38 (C_6H_6)	9.01	—	—		55
Me_2SnCl_2	—	8.83	—	—		34
Me_2SnCl_2	—	—	—	68.0, 71.0	110° C	176, 361
$\text{Me}_2\text{SnCl}_2/\text{acetone}$	—	—	—	—	$\mathcal{J}_{\text{Sn}^{119}\text{CH}_3} = 80$; $\delta_{\text{Me}_2\text{Sn}^{119}} = -36 \pm 2$	45
$\text{Me}_2\text{SnCl}_2/\text{H}_2\text{O}$	—	—	—	98 (Sn^{119})		45
Me_2SnH_2	—	9.80	—	57.6, 60.2	$\mathcal{J}_{\text{HSnCH}} = 2.65$; $\tau_{\text{SnH}} = 5.24$; $\mathcal{J}_{\text{SnH}} = 1717.4, 1797.1$; $\mathcal{J}_{\text{C}^{13}\text{H}} = 129.9$	64
$\text{Me}_2\text{Sn}(\text{CF}_3)\text{Cl}$	6.60 (C_6H_6)	9.23	—	—	$\delta_{\text{CF}_3\text{COOH}} = -28.2$	55
MeSnCl_3	—	8.35	—	—		34
MeSnCl_3	—	—	—	95.7, 100.0	55° C	176, 361
MeSnH_3	—	9.73	—	62	$\tau_{\text{SnH}} = 5.86$; $\mathcal{J}_{\text{C}^{13}\text{H}} = 130$; $\mathcal{J}_{\text{HSnCH}} = 2.7$; $\mathcal{J}_{\text{SnH}} = 1770, 1852$	127
Me_6Sn_2	—	9.81	—	46.2, 48.3	$\mathcal{J}_{\text{CH}_3-\text{Sn}-\text{Sn}} = 16.2$	182
Me_6Sn_2	—	9.78	—	46.4, 48.4	$\mathcal{J}_{\text{CH}_3\text{SnSn}} = 16.0$	35
$(\text{Me}_3\text{Sn})_2\text{O}$	—	9.73	—	—		34
$(\text{Me}_3\text{Sn})_2\text{O}$	—	9.78	—	53.6, 56.0		321
$(\text{Me}_3\text{Sn})_2\text{CH}_2$	—	9.94	—	50.7, 52.9	$\tau_{\text{CH}_2} = 10.28$; $\mathcal{J}_{\text{SnCH}_2} = 57.7, 60.3$	182
$\text{Me}_2\text{Sn}(\text{CF}_2\text{CF}_2\text{H})_2$	—	9.37	—	61.5, 64.5	See Table IV for $\text{CF}_2\text{CF}_2\text{H}$ group	64
$\text{Me}_2\text{SnH}(\text{CF}_2\text{CF}_2\text{H})$	—	9.69	—	60.1, 62.8	See Table IV for $\text{CF}_2\text{CF}_2\text{H}$ group	64
$(\text{Me}_3\text{Sn})_2\text{Se}$	—	9.434	—	53, 56		313
$\text{Me}_3\text{SnOSiMe}_3$	—	9.66	—	53.4, 55.8	$\tau_{\text{SiMe}_3} = 10.04$, $\mathcal{J}_{\text{Si}^{119}\text{CH}_3} = 6.72$	318, 319
$\text{Me}_3\text{SnN}(\text{SiMe}_3)_2$	—	9.69	—	53.4, 55.8	$\tau_{\text{SiMe}_3} = 9.98$; $\mathcal{J}_{\text{Si}^{119}\text{CH}_3} = 6.60$	318, 319
$\text{Me}_2\text{Sn}(\text{OSiMe}_3)_2$	—	9.44	—	68.0, 71.4	$\tau_{\text{SiMe}_3} = 9.98$	321
$\text{Me}_3\text{SnOSiMe}_3$	—	9.66	—	68.0, 71.4	$\tau_{\text{SiCH}_3} = 10.04$, $\mathcal{J}_{\text{Si}^{119}\text{Me}} = 6.72$	321

TABLE I—continued

Compound	δ (ppm)	τ (ppm)	Rel- ative inten- sity	\mathcal{J} (cps)	Remarks	References
(Me ₃ SnO) ₂ SiMe ₂	—	9.62	—	57.6, 60.0	$\tau_{\text{SiMe}} = 10.10$	321
MeSn(OSiMe ₃) ₃	—	9.35	—	—	$\tau_{\text{SiMe}} = 9.94$	321
Me ₃ SnSn(Me) ₂ SnMe ₃						
Chain end	—	9.73	—	45.8, 47.6	$\mathcal{J}_{\text{SnSnMe}} = 15.6$	35
Interior	—	9.60	—	42.8, 44.3	$\mathcal{J}_{\text{SnSnMe}} = 20.2$	
[Me ₂ Sn] _x linear						
Chain end	—	9.63	—	46.0, 48.0	$\mathcal{J}_{\text{SnSnMe}} = 15.7$	35
Interior	—	9.35	—	40.4	$\mathcal{J}_{\text{SnSnMe}} = 20.6$	
(Me ₂ Sn) ₆ cyclic	—	9.45	—	—	$\mathcal{J}_{\text{SnMe}} = 41.2$, $\mathcal{J}_{\text{SnSnMe}} = 20.6$, $\mathcal{J}_{\text{SnSnSnMe}} = 1.3$	35
Me ₃ Sn(C ₃ H ₅) <i>trans</i>	—	9.92	—	54	See Table VI for C ₃ H ₅	331
Me ₃ Sn(C ₃ H ₅) <i>cis</i>	—	9.85	—	—	See Table VI for C ₃ H ₅	331
Me ₄ Pb	4.04 (H ₂ O)	9.30	—	—		11, 296
Me ₄ Pb	— 34.0 cps (gaseous CH ₄)	—	—	—	$\delta_{\text{C}^{13}\text{H}_4} = 131.6$ ppm. Footnote b. $\mathcal{J}_{\text{C}^{13}\text{H}} = 133$	344
Me ₄ Pb	—	—	—	55.3		211
Me ₄ Pb	—	—	—	62.0	$\mathcal{J}_{\text{C}^{13}\text{H}} = 134$	233
Me ₃ PbH	—	9.15	—	67	$\tau_{\text{PbH}} = 2.32$, $\mathcal{J}_{\text{HPbMe}} = 1.5$, $\mathcal{J}_{\text{PbH}} = 2379$, $\mathcal{J}_{\text{C}^{13}\text{H}} = 136$	127
Me ₃ PbH	5.0 (CH ₂ Cl ₂)	9.7	—	68		101
Me ₄ Pb	—	9.27	—	61.0	$\mathcal{J}_{\text{C}^{13}\text{H}} = 135.3$	322
Me ₃ PbOSiMe ₃	—	8.79	—	69.5	$\tau_{\text{SiMe}} = 10.06$, $\mathcal{J}_{\text{C}^{13}\text{Me}} = 136.0$	322
Me ₃ PbOSiEt ₃	—	8.82	—	69.0	$\tau_{\text{SiCH}_3} = 9.63$, $\tau_{\text{SiCH}_2\text{CH}_3} = 9.09$, $\mathcal{J}_{\text{HCH}_3} = 8.0$	322

<i>Group V</i>						
Me ₃ N	3.18 (H ₂ O inf. diln)	8.4	—	—		8
Me ₃ P	4.30 (H ₂ O inf. diln)	9.5	—	—		8
Me ₃ As	4.39 (H ₂ O inf. diln)	9.6	—	—		8
Me ₃ Sb	4.53 (H ₂ O inf. diln)	9.7	—	—		8, 246
Me ₃ Bi	4.19 (H ₂ O inf. diln)	9.4	—	—		8, 246
<i>Group VI</i>						
Me ₂ Se	−0.54 (C ₆ H ₁₂)	8.0	—	11.2	$\mathcal{J}_{\text{C}^{13}\text{H}} = 140.2$	209
Me ₂ Te	—	—	—	20.7	$\mathcal{J}_{\text{C}^{13}\text{H}} = 140.5$	213
<i>Transition Metals</i>						
Me ₂ Zn	6.84 (C ₆ H ₆)	9.47	—	—		244
Me ₂ Cd	6.25 (C ₆ H ₆)	8.88	—	—		244
Me ₂ Cd ¹¹¹	—	—	—	50.2		209
Me ₂ Cd ¹¹³	1.80 (C ₆ H ₁₂)	10.4	—	50.2	$\mathcal{J}_{\text{C}^{13}\text{H}} = 126.2$	209
Me ₂ Hg	5.48 (C ₆ H ₆)	8.01	—	102		90, 246
Me ₂ Hg	5.46 (C ₆ H ₆)	8.09	—	—		244
Me ₂ Hg	—	9.714	—	102.5	Neat liquid	220a
MeHgCl	—	8.908	—	202.5	CH ₂ Cl ₂ soln	220a
MeHgCl	4.8 (C ₆ H ₆)	7.4	—	—	Inf diln	244
MeHgBr	4.7 (C ₆ H ₆)	7.3	—	—	Inf diln	244
MeHgI	4.6 (C ₆ H ₆)	7.2	—	—	Inf diln	244
MeHgI	0.317 (C ₆ H ₁₂)	8.877	—	200	Pyridine soln	160
MeHgClO ₄	—	8.79	—	260.2		220a
MeHgOAc	—	—	—	214.3	C ₆ H ₆ soln	160
				220.8	Pyridine soln	160
				233.4	D ₂ O soln	160
(MeHg) ₃ PO ₄	—	—	—	220.5	Pyridine soln	160
				233.2	D ₂ O soln	160
MeHgNO ₃	—	—	—	240.6	C ₆ H ₆ soln	160

TABLE I—*continued*

Compound	δ (ppm)	τ (ppm)	Rel- ative inten- sity	γ (cps)	Remarks	References
MeHgNO ₃	—	—	—	227.0	Pyridine soln	160
				259.2	D ₂ O soln	160
MeHgClO ₄	—	—	—	259.8	C ₆ H ₆ soln	160
				233.2	Pyridine soln	160
				259.6	D ₂ O soln	160
Me ₂ Hg	—	9.67	—	104.3	Pyridine soln	160
MeHgC ₂ H	—	9.415	—	150.6	Pyridine soln	160
(MeHg) ₂ S	—	9.31	—	156.6	Pyridine soln	160
MeHgCN	—	9.21	—	178.0	Pyridine soln	160
(MeHg) ₃ PO ₄	—	9.135	—	220.5	Pyridine soln	160
MeHgOAc	—	9.085	—	220.8	Pyridine soln	160
MeHgOH	—	9.002	—	214.2	Pyridine soln	160
MeHgCl	—	8.985	—	215.2	Pyridine soln	160
(MeHg) ₂ SO ₄	—	8.978	—	216.0	Pyridine soln	160
(MeHg) ₂ C ₂ O ₄	—	8.972	—	215.2	Pyridine soln	160
MeHgSCN	—	8.943	—	208.0	Pyridine soln	160
MeHgBr	—	8.937	—	212.0	Pyridine soln	160
MeHgNO ₃	—	8.922	—	227.0	Pyridine soln	160
MeHgClO ₄	—	8.730	—	233.2	Pyridine soln	160
Me ₂ Hg	—	—	—	100.6	C ₆ H ₆ soln	160
				104.3	Pyridine soln	160
MeHgCN	—	—	—	176.0	C ₆ H ₆ soln	160
				178.0	Pyridine soln	160
MeHgOH	—	—	—	204.0	C ₆ H ₆ soln	160
				214.2	Pyridine soln	160
(MeHg) ₂ SO ₄	—	—	—	205.0	C ₆ H ₆ soln	160
				216.0	Pyridine soln	160

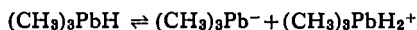
(MeHg) ₂ C ₂ O ₄	—	—	—	205.0 215.2	C ₆ H ₆ soln Pyridine soln	160 160
MeFe(CO) ₂ Cp	—	9.8	—	—	$\tau_{\text{CP}} \approx 5.6$	283
(Me ₃ PtI) ₄	—	—	—	77.9 77.7	± 1.0 , C ₆ H ₆ soln CHCl ₃ soln	343 343
(Me ₃ Pt)NO ₃	—	—	—	77.3	H ₂ O soln	343
[Me ₃ Pt·CH(COMe) ₂] ₂	—	—	—	78.9	C ₆ H ₆ soln	343
[Me ₃ Pt·CH(COEt) ₂] ₂	—	—	—	71.6	C ₆ H ₆ soln	343
[Me ₃ Pt·CH(COC ₃ H ₇) ₂] ₂	—	—	—	74.9	C ₆ H ₆ soln	343
Me ₂ Ptpy ₂ Cl ₂	—	—	—	83		343
Me ₄ Pt ₂ C ₈ H ₈						
Me	—	9.22	13	81		208
C ₈ H ₈	—	4.28	8	12, 26, 40	Seven bands	
Me ₂ PtC ₈ H ₁₂						
Me	—	9.19	8.5	86		208
CH	—	5.11	4.5	40		
CH ₂	—	7.62	9.2	18		
[(CO) ₂ MeFeC ₅ H ₄ CHNMe ₂] ₂						
FeMe	—	9.92	6	—		199b
NMe	—	7.88	12	—		
NCH	—	6.54	2	—		
C ₅ H ₄	—	5.3	8	—		
Me ₂ TiCp ₂	—	10.2	—	—	$\tau_{\text{CP}} \approx 4.1$	283
MeCr(NO) ₂ Cp	—	9.5	—	—	$\tau_{\text{CP}} \approx 5.2$	283
MeMo(CO) ₃ Cp	—	9.5	—	—	$\tau_{\text{CP}} \approx 5.2$	283
MeW(CO) ₃ Cp	—	9.6	—	—	$\tau_{\text{CP}} \approx 5.1$	285
MeMn(CO) ₅	—	10.1	—	—		

^a $\gamma_{\text{Ti}^{209}}\text{-CH}_3$ are 3.8 ± 0.3 less in each case.

^b 5 atm. compound and 5 atm. CH₄ or ¹³C₆H₆ at elevated temperature.

$(\text{CH}_3)_n\text{MCl}_{4-n}$ ($\text{M} = \text{C}, \text{Si}, \text{Sn}; n = 1-4$). They found that the position of the methyl resonance shifted more or less regularly to lower field as additional chlorine atoms were introduced. This is the result expected if the inductive effect of the highly electronegative chlorine atoms were predominant. (An upfield shift would be expected as the result of $d_\pi-p_\pi$ bonding, which returns electron density to the central atom.) However, the shift is less for silicon and tin than for carbon, which has no d orbitals available to partake in compensating $d_\pi-p_\pi$ double bonding, and least of all for silicon, which is best able to engage in this type of overlap with a chlorine atom. A somewhat analogous interaction between phenyl-group π electrons and silicon d orbitals was postulated (366) to account for observations on phenylmethylsilanes.

In the case of $(\text{CH}_3)_3\text{PbH}$ there appear to be some discrepancies. Duffy *et al.* (101) observed several minor absorptions which they considered to arise from the lead-bonded protons present in the equilibrium



More recently Flitcroft and Kaesz (127) have re-examined the spectrum, and were unable to detect several of the small peaks reported by the earlier workers. They have concluded that these peaks were due to impurities rather than the proposed equilibrium.

Ethyl Derivatives (Table II). In 1955, in an early application of high-resolution NMR spectroscopy, Dailey and Shoolery (79) studied the effect of various electron-withdrawing substituents on the proton spectrum of the ethyl group. One of the interesting findings of these authors was the existence of a straight-line correlation between the Pauling electronegativities of the halogens and the difference in chemical shift between the methyl and methylene protons ($\delta_{\text{CH}_3} - \delta_{\text{CH}_2} = \Delta\delta$) of the ethyl derivatives of these elements. Subsequent investigators have therefore tended to stress this quantity and its relation to the electronegativity of the substituent atom. More recently, Narasimhan and Rogers (267) have summarized the data for a number of ethyl derivatives of metals and metalloids and proposed slightly different constants for the equation when applied to these elements. Since there does seem to be an approximate correlation between $\Delta\delta$ and the ranges of electronegativities given to the elements by various authors, this quantity has been included in the Table.

Brownstein *et al.* (38), have used $\Delta\delta$ values in a study of the relative electron-withdrawing power of Al and Ga in the free triethyls and in their diethyl ether complexes. The data lead to the conclusions that the electron-

TABLE II
ETHYL DERIVATIVES

Compound	δ_{CH_3}	$\tau(\text{CH}_3)$	δ_{CH_2}	$\tau(\text{CH}_2)$	$\delta_{\text{CH}_2} - \delta_{\text{CH}_3}$	$\mathcal{J}_{\text{M-CH}_3}$	$\mathcal{J}_{\text{M-CH}_2}$	$\mathcal{J}_{\text{CH}_2-\text{CH}_3}$	Remarks	References
<i>Group I</i>										
EtLi	5.93 (C_6H_6)	8.6	8.12 (C_6H_6)	10.8	-2.19	~ 0	~ 0	8.4	Li^{17} : $\delta_{70\% \text{LiBr}} = -1.00$; $\delta_{7\% \text{LiBr}} = -1.28$	36
EtLi	—	—	—	10.99	—	0	0	8.9	5% in ether	128
<i>Group II</i>										
EtMgBr	—	—	—	10.62	—	—	—	8.96	5% in ether	128
Et ₂ Mg/Et ₂ O	—	8.840	—	10.84	—	—	—	—	Satd soln in dioxane, conc dependent	220a
EtMgBr/Et ₂ O	—	8.806	—	10.62	—	—	—	—	0.020 M conc dependent	220a
<i>Group III</i>										
Et ₃ B	—	—	—	—	—	—	—	—	$\delta_{\text{B}^{11}(\text{OME})_3} = -66.6$	282
Et ₃ B	—	—	—	—	—	—	—	—	Et-mult., approx. center $\tau = 8.91$; $\delta_{\text{B}^{11}\text{F}_3\text{OEt}_2} = -85$	140
EtBCl ₂	—	—	—	—	—	—	—	—	$\delta_{\text{B}^{11}\text{Cl}_2} = -16.0$	72
EtBF ₂	—	—	—	—	—	—	—	—	$\delta_{\text{B}^{11}\text{Cl}_2} = 18.9$	72
EtBF ₂	—	—	—	—	—	—	—	—	$\delta_{\text{CCl}_3\text{F}} = 78.4$ (neat), 74.6 (inf diln); $\mathcal{J}_{\text{B}^{11-\text{F}}} = 81$	74
Et ₃ Al	—	—	—	—	-0.71	—	—	7.9		38
Et ₃ Al·OEt ₂	—	—	—	—	-1.02	—	—	6.0		38
Et ₃ Al·OEt ₂	—	—	—	—	2.25	—	—	5.8	Footnote a	38
Et ₂ AlCl	4.2 (H_2O)	9.4	4.6 (H_2O)	9.8	-0.4	—	—	—		21
Et ₂ AlH·NMe ₃	0.35 (C_6H_{12})	8.91	1.59 (C_6H_{12})	10.15	—	—	—	—	$\delta_{\text{NCH}_3} = -0.94$ $\tau_{\text{NCH}_3} = 7.62$	281
EtAlH ₂ ·NMe ₃	0.47 (C_6H_{12})	9.03	1.64 (C_6H_{12})	10.20	—	—	—	—	$\tau_{\text{H}} = 6.46$; $\tau_{\text{NCH}_3} = 7.52$	281
Et ₃ Al·N ₂ Me ₄	1.54	—	2.72	—	—	—	—	8.1	Shifts relative to Me ₂ NNMe ₂ group of complex	65
Et ₂ AlClN ₂ Me ₄	1.54	—	2.58	—	—	—	—	7.9	Shifts relative to Me of (Me ₂ N) ₂ of complex	65
[EtAlCl ₂ NHNMe ₂] ₂	0.92	—	1.98	—	—	—	—	—	$\delta_{\text{NH}} = -0.09$; $\delta_{\text{NCH}_3} = 0$	65
EtAlCl ₂ N ₂ Me ₄	1.59	—	2.47	—	—	—	—	—	$\delta_{\text{NCH}_3} = 0$	65
[EtAlClNHNMMe ₂] ₂	0.92	—	1.98	—	—	—	—	—	$\delta_{\text{NCH}_3} = 0$; $\delta_{\text{NH}} = -0.09$	65
[EtAlOSiMe ₃] ₂	—	9.17	—	10.14	—	—	—	—	$\tau_{\text{SiMe}_3} = 9.73$	319
Et ₃ Ga	—	—	—	—	-0.50	—	—	7.9		38
Et ₃ Ga·OEt ₂	—	—	—	—	-0.58	—	—	5.4		38
Et ₃ Ga·OEt ₂	—	—	—	—	2.12	—	—	5.0	Footnote a	38
[Et ₂ Tl] ₂ CO ₃	—	—	—	—	0.29	338.0	623.0	7.6	D ₂ O $\mathcal{J}_{\text{Tl}^{203}\text{CH}_3} 3.4 \pm 0.3$ cps	159
	-0.63 (C_6H_{12})	7.93	Unobs.	—	—	358.0	—	7.6	Pyridine less than value	

TABLE II—continued

Compound	δ_{CH_3}	$\tau(\text{CH}_3)$	δ_{CH_2}	$\tau(\text{CH}_2)$	$\delta_{\text{CH}_2} - \delta_{\text{CH}_3}$	$J_{\text{M}-\text{CH}_2}$	$J_{\text{M}-\text{CH}_3}$	$J_{\text{CH}_2-\text{CH}_3}$	Remarks	References
Et ₃ Tl lactate	—	—	—	—	0.28	338.0	623.0	7.6	D ₂ O given for Tl ²⁰⁵	159
	-0.31 (C ₆ H ₁₂)	8.25	-0.62	7.94	—	359.0	620.0	7.6	Pyridine	
Et ₃ TlSCN	—	—	—	—	0.33	337.0	623.0	7.6	D ₂ O $J_{\text{Tl}-\text{CH}_3}$ 6.3 ± 0.3 cps	159
	-0.31 (C ₆ H ₁₂)	8.25	-0.78	7.78	—	361.0	628.0	7.6	Pyridine less than value	
Et ₃ TlClO ₄	—	—	—	—	0.30	337.0	623.0	7.6	D ₂ O given for Tl ²⁰⁵	159
	-0.23 (C ₆ H ₁₂)	8.33	-0.97	7.59	—	366.0	638.0	7.6	Pyridine	
Et ₃ TlNO ₃	—	—	—	—	0.40	338.0	623.0	7.6	D ₂ O	159
	-0.29 (C ₆ H ₁₂)	8.27	-0.83	7.63	—	373.0	630.0	7.6	Pyridine	
Et ₃ Tl	—	8.21	—	8.71	-0.50	198	396	7.7		221
Et ₃ TlMe	—	8.18	—	8.71	-0.53	219	441	7.7	$J_{\text{Tl}-\text{CH}_3}$, $J_{\text{Tl}-\text{CH}_3}$ of opposite sign;	221
EtTlMe ₂	—	8.20	—	8.66	-0.46	242	473	7.7	see Table I for methyl group	221
<i>Group IV</i>										
Et ₄ Si	-54.0 cps (gaseous CH ₄)	—	-34.0 cps (gaseous CH ₄)	—	—	—	—	—	$\delta_{\text{C}^{13}\text{H}_4} = 128.8$ (CH ₃), 117.7 (CH ₂); footnote b	344
Et ₄ Si	3.80 (H ₂ O)	9.0	4.22 (H ₂ O)	9.4	-0.42	—	—	7.9		248
Et ₃ SiF	—	—	—	—	—	—	—	—	$\delta_{\text{CCl}_3\text{F}} = 176.2$	112
Et ₃ SiCl	—	—	—	—	-0.015	—	—	—		267
EtSiCl ₃	—	—	—	—	-0.019	—	—	8.0		267
Et ₄ Ge	—	—	—	—	-0.307	—	—	7.8		267
Et ₄ Sn ¹¹⁷	—	—	—	—	-0.390	~ 30.8	~ 68.1	~ 8.2	$J_{\text{Sn}-\text{CH}_3}$, $J_{\text{Sn}-\text{CH}_3}$ of opposite sign	265
Et ₄ Sn ¹¹⁹	—	—	—	—	-0.390	32.2	71.2	8.2	$J_{\text{Sn}-\text{CH}_3}$, $J_{\text{Sn}-\text{CH}_3}$ of opposite sign	265
Et ₄ Sn ¹¹⁷	—	—	—	—	—	49.1	66.8	—		209
Et ₄ Sn ¹¹⁹	0.26 (C ₆ H ₁₂)	8.8	0.64 (C ₆ H ₁₂)	9.2	-0.37	51.4	69.8	7.9		209
Et ₄ Sn	—	—	—	—	—	—	—	—	$\delta_{\text{C}^{13}\text{H}_4} = 126.7$ (CH ₂), 122.5 (CH ₃); footnote b	344
Et ₃ Sn ¹¹⁷ Cl ₂	—	—	—	—	-0.36	—	131.7	7.9		134
Et ₃ Sn ¹¹⁹ Cl ₂	—	—	—	—	-0.36	—	137.8	7.9		134
Et ₃ Sn ¹¹⁷ (OMe) ₂	—	—	—	—	0.057	70.5	117.4	8.0		134
Et ₃ Sn ¹¹⁹ (OMe) ₂	—	—	—	—	0.057	73.6	122.9	8.0		134
Et ₄ Pb	—	—	—	—	~ 0	41.0	125	8.2	$J_{\text{Pb}-\text{CH}_3}$, $J_{\text{Pb}-\text{CH}_3}$ of opposite sign	265
Et ₄ Pb	3.2 (H ₂ O)	8.4	3.2 (H ₂ O)	8.4	0	31	135	—		21
Et ₄ Pb	-44.5 cps (gaseous CH ₄)	—	-44.5 cps (gaseous CH ₄)	—	0	—	—	—	$\delta_{\text{C}^{13}\text{H}_4} = 117.9$ (CH ₂), 112.8 (CH ₃); footnote b	344

<i>Group V</i>									
Et ₃ P	—	—	—	—	0.292	0.5	13.7	7.6	$\mathcal{J}_{P-CH_3}, \mathcal{J}_{P-CH_3}$ of opposite sign 265
<i>Group VI</i>									
Et ₃ Se	0.0 (C ₆ H ₁₂)	8.6	-1.45 (C ₆ H ₁₂)	7.1	1.45	< 15	< 15	7.0	209
Et ₃ Te	—	—	—	—	1.00	—	—	7.0	213
<i>Group VII</i>									
EtF	—	8.76	—	5.64	3.12	46.7	25.2	6.9	$\mathcal{J}_{F-CH_3}, \mathcal{J}_{F-CH_3}$ of same sign 347
<i>Transition Metals</i>									
Et ₃ Zn	—	—	—	—	-0.848	—	—	8.6	267
Et ₃ Cd ¹¹¹	—	—	—	—	—	49.4	57.2	—	267
Et ₃ Cd ¹¹³	0.15 (C ₆ H ₁₂)	8.7	0.91 (C ₆ H ₁₂)	9.5	-0.76	51.2	59.8	8.2	267
Et ₂ Hg	4.75 (C ₆ H ₆)	7.4	5.00 (C ₆ H ₆)	7.6	-0.25	91	120	7.5	$\delta_{Me_2^{199}Hg} = 33.0$ 90
Et ₂ Hg	—	—	—	—	-0.240	87.6	115.2	7.0	$\mathcal{J}_{Hg-CH_3}, \mathcal{J}_{Hg-CH_3}$ of opposite sign 264, 266
Et ₂ Hg	—	8.706	—	8.996	—	—	—	—	CH ₂ Cl ₂ soln 220a
Et ₂ Hg	0.06 C ₆ H ₁₂)	8.62	0.375 (C ₆ H ₁₂)	8.93	—	100.1	127.5	—	Pyridine soln; \mathcal{J} 's solvent dependent 160
EtHgCl	—	8.652	—	8.026	—	—	—	—	CH ₂ Cl ₂ soln 220a
EtHgCl	+0.10 (C ₆ H ₁₂)	8.66	-0.470 (C ₆ H ₁₂)	8.09	—	216.0	296.0	—	Pyridine soln; \mathcal{J} 's solvent dependent 160
EtHgBr	—	8.635	—	7.979	—	—	—	—	CH ₂ Cl ₂ soln 220a
EtHgBr	+0.063 (C ₆ H ₁₂)	8.62	-0.517 (C ₆ H ₁₂)	8.04	—	213.8	301.0	—	Pyridine soln; \mathcal{J} 's solvent dependent 160
EtHgI	—	8.571	—	7.897	—	—	—	—	CH ₂ Cl ₂ soln 220a
EtHgClO ₄	—	8.69	—	7.71	—	—	—	—	D ₂ O soln 220a
EtHgCN	+0.02 (C ₆ H ₁₂)	8.58	-0.260 (C ₆ H ₁₂)	8.30	—	186.0	222.0	—	Pyridine; \mathcal{J} 's solvent dependent 160
EtHgNO ₃	0 (C ₆ H ₁₂)	8.56	-0.650 (C ₆ H ₁₂)	7.91	—	233.0	311.0	—	Pyridine; \mathcal{J} 's solvent dependent 160
CpFe(CO) ₂ Et	—	—	—	—	—	—	—	—	Center of Et resonance at $\tau = 8.59$, 12 peaks, $\tau_{CD} = 5.40$ 144
Mn(CO) ₅ Et	—	—	—	—	—	—	—	—	Center of Et resonance at $\tau = 8.69$, six peaks 144

^a For neat Et₂O: ($\delta_{CH_2} - \delta_{CH_3}$) = 2.50, $\mathcal{J}_{CH_2-CH_3}$ = 7.1 (142).

^b 5 Atm compound and 5 atm CH₄ or C₆¹³H₆ at elevated temperature.

withdrawing power of the metal atom is less in the complex, and that gallium is more electronegative than aluminum. The first conclusion is amply supported by theory and observation, but there will be many who will question the second statement, even though the evidence for electronegativity alternation is growing (8, 11, 267).

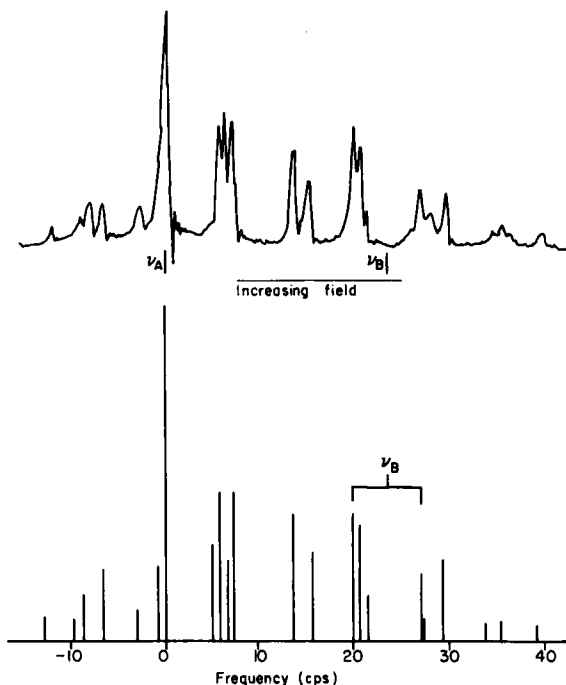


FIG. 1. Proton NMR spectrum of tin tetraethyl at 60 Mc/sec (main multiplet only). The calculated spectrum (bottom) is the theoretical A_3B_2 spectrum with $[\mathcal{J}_{AB}/\delta_{AB}] = 0.350$, after Narasimhan and Rogers (265) (reproduced with permission).

Since the difference in chemical shift between the methyl and methylene protons of an ethyl group is generally of the same order of magnitude as the spin-spin coupling constant (with presently available spectrometer frequencies), these spectra tend to be of the type described as A_3B_2 systems (Figs. 1 and 2). One consequence of the second-order spectra thus obtained has been to permit the ready calculation of relative signs of the spin-spin coupling constants of the protons with a magnetically active nucleus to which the group is bound. Thus, analysis of the spectra of ethyl derivatives of Sn^{117} , Sn^{119} , Pb^{207} , P^{31} , and Hg^{199} showed that in each case the $\text{CH}_3\text{—M}$

and $\text{CH}_2\text{—M}$ coupling constants were of opposite sign (265). By an elegant double resonance technique, Maher and Evans demonstrated that the same is true for an ethyl group bonded to the Tl^{205} nucleus (221). It has more recently been shown to be true also for ethyl groups bonded to C^{13} and N^{14} (14, 185). The only exception to this rule so far found is F^{19} , analysis of the

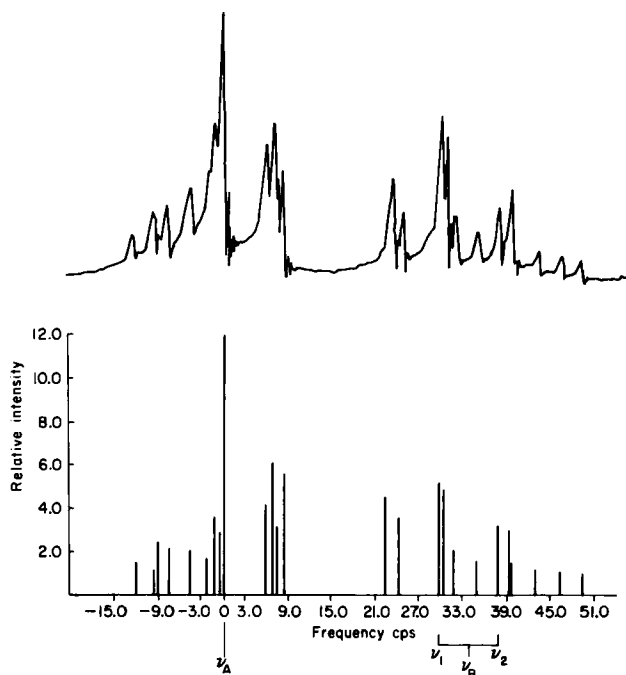


FIG. 2. Experimental (top) and theoretical (bottom) proton NMR spectrum of zinc diethyl at 40 Mc/sec; the theoretical spectrum is calculated for $\delta = -33.9$ cps and $\mathcal{J} = 8.6$ cps, after Narasimhan and Rogers (267) (reproduced with permission).

ethyl fluoride spectrum indicating that $\mathcal{J}_{\text{CH}_3\text{—F}}$ and $\mathcal{J}_{\text{CH}_2\text{—F}}$ have the same sign (347).

A second generalization which can be made regarding these couplings in ethyl metal compounds is that $\mathcal{J}_{\text{CH}_3\text{—M}} > \mathcal{J}_{\text{CH}_2\text{—M}}$. Again, $\text{C}_2\text{H}_5\text{—C}^{13}$ and $\text{C}_2\text{H}_5\text{—N}^{15}$ obey the rule, but $\text{C}_2\text{H}_5\text{—F}^{19}$ does not. Theories which have been presented so far to explain this somewhat surprising relative magnitude of \mathcal{J} 's do not satisfactorily account for both the adherence of C^{13} and N^{14} to the trend, and the deviation of F^{19} from it.

Miscellaneous Alkyl Derivatives (Table III). Data for a number of metal

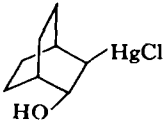
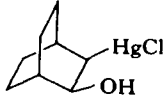
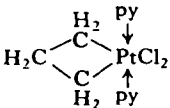
TABLE III
MISCELLANEOUS ALKYL DERIVATIVES

Compound	δ (ppm)	τ (ppm)	\mathcal{J} (cps)	Remarks	References	
<i>Group I</i>						
(<i>n</i> -BuLi) ₂ OEt ₂						
CH ₂ /Bu	—	10.98	—		60	
CH ₂ /Et	—	6.37	—			
Me ₃ CLi	—	9.01	—		368	
<div><div><div><div><div>H_b</div><div>H_a</div></div><div><div>C</div><div>C</div></div><div><div>H_x</div><div>Li</div></div></div><div><div>C</div><div>C</div></div><div><div>H_b</div><div>H_a</div></div></div></div>	H _a H _b H _x	0.05 (C ₃ H ₆) —0.46 (C ₃ H ₆) 2.5 (C ₃ H ₆)	9.83 9.32 12.28	\mathcal{J}_{ax} 9.5 \mathcal{J}_{bx} 11.5 —	THF soln Further 1 cps splitting of a and b resonances	330
<i>Group II</i>						
CH ₃ CHCH ₂ CH ₃ MgBr						
CH ₃	—	8.5	6.8	5% in ether	128	
CHCH ₂	—	10.20	—			
CH ₃ CHCH ₂ MgBr						
ϕ						
(A) CH ₃	—	8.77	$\mathcal{J}_{BC} = 6.6$	8% in ether	128	
(B) CH	—	7.06	$\mathcal{J}_{AB} = 6.5$			
(C) CH ₂	—	10.00				
ϕ CH ₂ CHCH ₃						
MgBr						
(A) CH ₂	—	7.33	$\mathcal{J}_{BC} = 7.4$	5% in ether	128	
(B) CH	—	9.81	$\mathcal{J}_{AB} = 7.4$			
(C) CH ₃	—	8.75				

$n\text{-C}_3\text{H}_7\text{BF}_2$	—	—	$\mathcal{J}_{\text{B}^{11}\text{-F}} = 81$	$\delta_{\text{CCl}_3\text{F}} = 75.8$ (neat) $= 72.8$ (inf diln)	74
<i>tert</i> -BuB(<i>i</i> -Bu) ₂					
CH ₃ (<i>tert</i>)	4.18 (H ₂ O)	9.4	—		
CH ₃ (<i>i</i>)	4.10, 4.25 (H ₂ O)	9.3, 9.5	—		81
CH ₂ (<i>i</i>)	3.78, 3.95 (H ₂ O)	9.0, 9.2	—		
(<i>i</i> -Bu) ₃ B					
CH ₃	4.15, 4.30 (H ₂ O)	9.4, 9.5	—		81
CH ₂	3.80, 3.98 (H ₂ O)	9.0, 9.2	—		
(<i>i</i> -Bu) ₃ Al					
CH ₃	9.1	—	—		175
CH ₂	9.7	—	—		
CH	8.1	—	—		
<i>Group IV</i>					
(<i>n</i> -C ₃ H ₇) ₄ Sn	—	—	$\mathcal{J}_{\text{Sn-}\alpha} = 49.1$ $\mathcal{J}_{\text{Sn-}\beta} = 67.2$ $\mathcal{J}_{\text{CH}_3\text{-}\beta} \sim 7.8$ $\mathcal{J}_{\alpha\text{-}\beta} = 7.5$	$\delta_{\text{CH}_3} - \delta_\beta = 0.75$ $\delta_\beta - \delta_\alpha = -0.54$	212
(<i>n</i> -C ₃ H ₇) ₄ Pb	—	—	$\mathcal{J}_{\text{Pb-}\alpha} = 40.5$ $\mathcal{J}_{\text{Pb-}\beta} = 102.4$ $\mathcal{J}_{\text{CH}_3\text{-}\beta} \sim 7.3$ $\mathcal{J}_{\alpha\text{-}\beta} = 7.5$	$\delta_{\text{CH}_3} - \delta_\beta = 0.55$ $\delta_\beta - \delta_\alpha = -0.34$	212
<i>Transition Metals</i>					
(<i>n</i> -C ₃ H ₇) ₂ Cd	—	—	$\mathcal{J}_{\text{Cd-}\alpha} = 51.6$ $\mathcal{J}_{\text{Cd-}\beta} = 60.2$ $\mathcal{J}_{\text{CH}_3\text{-}\alpha} \sim 7.4$ $\mathcal{J}_{\alpha\text{-}\beta} = 7.4$	$\delta_{\text{CH}_3} - \delta_\beta = 0.68$ $\delta_\beta - \delta_\alpha = -0.97$	212
(CH ₂) ₃ [FeCp(CO) ₂] ₂					
Cp	—	5.36	—		194
CH ₂	—	8.58	—		
(CH ₂) ₄ [FeCp(CO) ₂] ₂					
Cp	—	5.35	—		194
CH ₂	—	8.65	—		

TABLE III—continued

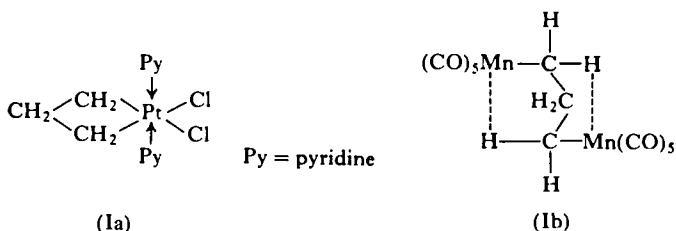
Compound	δ (ppm)	τ (ppm)	γ (cps)	Remarks	References
(CH ₂) ₅ [FeCp(CO) ₂] ₂					
Cp	—	5.36	—		194
CH ₂	—	8.60	—		
(CH ₂) ₆ [FeCp(CO) ₂] ₂					
Cp	—	5.35	—		194
CH ₂	—	8.64	—		
(CCH ₂) ₂ [FeCp(CO) ₂] ₂					
Cp	—	5.28	—		194
CH ₂	—	8.30	—		
Cp ₍₁₎ Fe(CO) ₂ (CH ₂) ₃ -COFe(CO) ₂ Cp ₍₂₎					
Cp ₍₁₎	—	5.27	—		192
Cp ₍₂₎	—	5.17	—		
CH ₂ CO	—	7.09	—	Rel intensity 2	
(CH ₂) ₂	—	8.61	—	Rel intensity 4	
CH ₃ COFe(CO) ₂ Cp					
Cp	—	5.13	—		192
CH ₃	—	7.43	—		
Me ₂ NCOFe(CO) ₂ Cp					
Cp	—	5.12	—		192
CH ₃	—	7.02	—		
(CH ₂) ₃ [Mn(CO) ₅] ₂	—	5.14	8	See text p. 26	192a
		6.32	—		
		8.04	—		
(CH ₃ CH ₂) ₂ NCOFe(CO) ₂ Cp					
Cp	—	5.15	—		192
CH ₂	—	6.57	7		
CH ₃	—	8.91	—		

$\text{CH}_3\text{C}_3\text{H}_5[\text{Mn}(\text{CO})_5]_2$	—	4.9	—	Complex mult	192a
		6.3	—	Complex mult	
		7.9	7	Complex mult	
		8.44	—	Doublet	
	—	8.33	—	CDCl_3 soln	355
		5.64	—		
		7.3	—		
		8.11	—		
	—	8.32	—	CDCl_3 soln	355
	—	5.65	—		
	—	6.73	—		
		7.28	—		
$(i\text{-C}_3\text{H}_7)_2\text{Hg}$					
CH	4.85 (C_6H_6)	7.5	$\mathcal{J}_{\text{Hg-CH}} = 78$	$\text{Hg}^{199}: \delta_{\text{Me}_2\text{Hg}} = 64.0$	90
CH_3	4.85 (C_6H_6)	7.5	$\mathcal{J}_{\text{Hg-CH}_3} = 126$		
$(n\text{-C}_3\text{H}_7)_2\text{Hg}$					
α	5.15 (C_6H_6)	7.8	$\mathcal{J}_{\text{Hg-}\alpha} = 90$	$\text{Hg}^{199}: \delta_{\text{Me}_2\text{Hg}} = 24.0$	90
β	4.20 (C_6H_6)	6.8	$\mathcal{J}_{\text{Hg-}\beta} = 108$		
$(n\text{-C}_3\text{H}_7)_2\text{Hg}$	—	—	$\mathcal{J}_{\text{Hg-}\alpha} = 95.0$	$\delta_{\text{CH}_3} - \delta_\beta = 0.89$	212
			$\mathcal{J}_{\text{Hg-}\beta} = 110.3$	$\delta_\beta - \delta_\alpha = -0.76$	
			$\mathcal{J}_{\text{CH}_3-\beta} \sim 7.2$		
			$\mathcal{J}_{\alpha-\beta} = 7.2$		
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{HgCOCH}_3\text{OCH}_3$	1.4 (H_2O)	6.6	$\mathcal{J}_{\alpha-\beta} \sim 7$		68
β	1.1 (H_2O)	6.3	—		
α	2.6 (H_2O)	7.8	—		
COCH_3	2.8 (H_2O)	8.0	—		
$\text{HOCH}_2\text{CH}_2\text{HgOH}$					
COH	-0.1 (H_2O)	5.1	$\mathcal{J}_{\alpha-\beta} \sim 8$		See also 370
β	0.8 (H_2O)	6.0	—		68
α	1.8 (H_2O)	7.0	—		
	—	~ 7.5	$\mathcal{J}_{\alpha-\beta} = 7.5$		3
			$\mathcal{J}_{\text{Pt}^{195}\text{-H}} = 83$		

derivatives in which the alkyl group is longer or of greater complexity than an ethyl group is gathered in Table III.

It may be noted that in propyl derivatives, as in ethyl derivatives, coupling with a magnetically active nucleus is greater in magnitude for protons on the β carbon than for protons on the α carbon. The relative signs of the coupling constants have not been determined in this case, but they may be assumed to be opposite by analogy with that in the ethyl derivatives.

In this section, two compounds deserve further comment. The compound



(Ia) is the adduct of a platinum salt with cyclopropane. It was suggested that the cyclopropane ring in this (and in related compounds) remained intact, acting as a pseudo- π -donor in a manner analogous to ethylene. The proton resonance spectrum, however, consists of a single peak representing all the protons which are accidentally coincident in chemical shift (3, 4). Also, satellite triplets arising from $\text{Pt}^{195}\text{—H}$ spin-spin coupling were observed, from which it was deduced that a $\text{CH}_2\text{—Pt}$ bond must be present in the structure indicated above.

For the derivative (Ib), an unusual proton resonance spectrum for the trimethylene group bridging the two metal atoms was obtained (192a). The only structure in agreement with all the data is the one shown above, which was put forth by the author. This is certainly one problem which is worthy of further attention since a most unusual role for the methylene hydrogen is postulated.

Fluoroalkyl Derivatives (Table IV). The F^{19} magnetic resonance spectra available for fluoroalkyl metal compounds thus far are mainly for derivatives of transition metals, only a few spectra having yet been reported for the many known derivatives of the main group elements.

The only main group derivatives in which NMR appears to have played a role in structure determination are the CF_3BF_3^- anion (54) and in the fluoroalkyl derivatives of tin (64). For CF_3BF_3^- , the spectrum revealed coupling

TABLE IV
FLUOROALKYL DERIVATIVES

Compound	α^a		β^a		γ^a		Spin-spin couplings	Remarks	References
	δ	ψ	δ	ψ	δ	ψ			
<i>Group III</i>									
CF_3BF_3^-	-2.06 (CF_3COOH)	74.5	—	—	—	—	$J_{\beta-\alpha} = 34$, $J_{\beta-\text{BF}} = 39$, $J_{\text{BF}-\text{CF}} = 0$	$\delta_{\text{CF}_3\text{COOH}} 77.3$ (BF_3^-) ($\psi = 154$)	54
<i>Group IV</i>									
CF_3SnMe_3	29.1 (CF_3COOH)	105.7	—	—	—	—		See Table I for methyl groups	55
$\text{CF}_3\text{SnMe}_2\text{Cl}$	28.2 (CF_3COOH)	104.8	—	—	—	—			55
$\text{C}_3\text{F}_5\text{Sn}(\text{C}_3\text{H}_5)_3$	—	120.3	—	84.4	—	—			285
$\text{C}_3\text{F}_5\text{Sn}(\text{C}_4\text{H}_9)_3$	—	120.4	—	83.9	—	—	$J_{\alpha-\beta} = 1.4$		285
$(\text{C}_3\text{F}_5)_3\text{Sn}(\text{CH}_3)_3$	—	118.9	—	83.7	—	—			285
$\text{C}_3\text{F}_7\text{Sn}(\text{C}_4\text{H}_9)_3$	—	118.2	—	122.7	—	80.3	$J_{\alpha-\gamma} = 9.5$		285
$\text{Me}_2\text{Sn}(\text{CF}_3\text{CF}_2\text{H})_2$	37.9 (CF_3COOH)	114.5	51.2 (CF_3COOH)	127.8	—	—	$J_{\text{SnF}\alpha} = 274 \pm 10$; $J_{\text{SnF}\beta} = 8 \pm 1$; $J_{\text{HFA}} = 5.1$; $J_{\text{HFB}} = 56.7$		64
$\text{Me}_2\text{SnH}(\text{CF}_3\text{CF}_2\text{H})$	38.2 (CF_3COOH)	114.8	51.2 (CF_3COOH)	127.8	—	—	$J_{\text{SnHFA}} = 8.3$; $J_{\text{SnHFB}} = 2.65$; $J_{\text{CHF}\alpha} = 5.6$; $J_{\text{CHF}\beta} = 57.0$ $J_{\text{SnF}\alpha} = 240$, 251 ± 2 ; $J_{\text{SnF}\beta} = 20 \pm 1$		64
<i>Group V</i>									
$(\text{C}_3\text{F}_7)_3\text{PI}$	—	102.9	—	119.7	—	81.2	$J_{\alpha-\beta} = 3.2$; $J_{\alpha-\gamma} = 9.2$; $J_{\text{F}-\alpha} = 23.6$; $J_{\text{F}-\beta} = 36.2$; $J_{\text{F}-\gamma} = 9.2$		285
$(\text{C}_3\text{F}_7)_3\text{PCl}$	—	120.1	—	122.7	—	81.2	$J_{\alpha-\gamma} = 9.6$; $J_{\text{F}-\alpha} = 58.4$; $J_{\text{F}-\beta} = 36.5$; $J_{\text{F}-\gamma} = 9.6$		285
<i>Transition Metals</i>									
$(\text{HCF}_2\text{CF}_2)\text{Mo}(\text{CO})_3\text{Cp}$	—	59.9	—	128.0	—	—	$J_{\alpha-\beta} < 1$; $J_{\alpha-\text{H}} < 1$; $J_{\beta-\text{H}} = 58$		285, 358

TABLE IV—continued

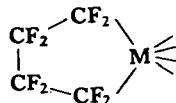
Compound	α^a		β^a		γ^a		Spin-spin couplings	Remarks	References
	δ	ψ	δ	ψ	δ	ψ			
(HCF ₂ CF ₂)W(CO) ₅ Cp	—	57.1	—	123.4	—	—	$J_{\alpha-\beta} = 3.1$; $J_{\alpha-H} = 3.1$; $J_{\beta-H} = 57$		358, 285
(CF ₃) ₃ [Mn(CO) ₅] ₂	—	55	—	99	—	—	2		192a
(CO) ₅ MnCO(CF ₃) ₂ COMn(CO) ₅	—	109	—	121	—	—	—		192a
CF ₃ Mn(CO) ₅	—85.8 (CF ₃ COOH)	—9.2	—	—	—	—	—		237
C ₂ F ₅ Mn(CO) ₅	—	68.8	—	84.0	—	—	$J_{\alpha-\beta} = 1.5$		285
C ₂ F ₅ COMn(CO) ₅	—	114.5	—	80.3	—	—	$J_{\alpha-\beta} = 0.7$		285
(CF ₃) ₂ CFMn(CO) ₅	87.1 (CF ₃ COOH)	163.7	—8.9 (CF ₃ COOH)	67.7	—	—	—		237
n-C ₂ F ₇ Mn(CO) ₅	—11.3 (CF ₃ COOH)	65.3	37.6 (CF ₃ COOH)	114.2	0.45 (CF ₃ COOH)	77.0	$J_{\alpha-\gamma} = 8$	α, β -assignments reversed in reference	237
C ₃ F ₇ Mn(CO) ₅	—	65.6	—	115.3	—	78.8	$J_{\alpha-\gamma} = 12.4$		285
HCF ₂ CF ₂ Mn(CO) ₅	—	59.8	—	121.5	—	—	$\tau = 4.68$; $J_{\alpha-\beta} < 1$; $J_{\alpha-H} = 5.3$; $J_{\beta-H} = 58$		315
HCF ₂ CF ₂ COMn(CO) ₅	—	117.5	—	139.8	—	—	$\tau = 4.14$; $J_{\alpha-\beta} = 9.2$; $J_{\alpha-H} = 6.7$; $J_{\beta-H} = 52$		315
HCClFCF ₂ Mn(CO) ₅	—	53.1 ^b	—	138.4	—	—	$\tau = 4.17$; $J_{\alpha-\beta} = 16.4, 12.4$; $J_{\alpha-H} = 12.4, 5.7$; $J_{\beta-H} = 52$		315
HCCl ₂ CF ₂ Mn(CO) ₅	—	45.8	—	—	—	—	$\tau = 4.30$; $J_{\alpha-H} = 10.5$		315
H(CF ₃) ₄ COMn(CO) ₅	51.8 (CF ₃ COOH)	128.4	33.6 (CF ₃ COOH)	110.2	46.2 (CF ₃ COOH)	122.8	$J_{\delta-H} = 50$	$\delta_{\delta-CF_3} = 60.8$ (CF ₃ COOH) ($\psi = 137.4$) δ_{β} and δ_{γ} assign- ments uncertain	237
C ₂ F ₅ Re(CO) ₅	—	74.9	—	84.2	—	—	$J_{\alpha-\beta} = 1.9$		285
C ₃ F ₇ Re(CO) ₅	—	72.7	—	115.1	—	78.5	$J_{\alpha-\gamma} = 12.3$		285
C ₂ F ₅ CORE(CO) ₅	—	116.7	—	80.5	—	—	$J_{\alpha-\beta} = 0.7$		285
C ₃ F ₇ CORE(CO) ₅	—	113.7	—	126.7	—	81.0	$J_{\alpha-\gamma} = 9.3$		285

$\text{CF}_3\text{Fe}(\text{CO})_4\text{I}$	—	14.7	—	—	—	—	—	285
$(\text{C}_3\text{F}_5)_2\text{Fe}(\text{CO})_4$	—	74.0	—	83.7	—	—	$\mathcal{J}_{\alpha-\beta} = 2.0$	285
$\text{C}_3\text{F}_5\text{Fe}(\text{CO})_4\text{I}$	—	59.0	—	83.5	—	—	$\mathcal{J}_{\alpha-\beta} = 1.8$	285
$(\text{C}_3\text{F}_7)_2\text{Fe}(\text{CO})_4$	—	69.1	—	115.3	—	78.6	$\mathcal{J}_{\alpha-\gamma} = 11.1$	285
$\text{C}_3\text{F}_7\text{Fe}(\text{CO})_4\text{I}$	—	54.9	—	114.4	—	78.2	$\mathcal{J}_{\alpha-\gamma} = 11.4$	285
$(\text{HCF}_2\text{CF}_2)_2\text{Fe}(\text{CO})_4$	—	66.1	—	124.7	—	—	$\mathcal{J}_{\alpha-\beta} < 1$; $\mathcal{J}_{\alpha-\text{H}} < 1$; $\mathcal{J}_{\beta-\text{H}} = 57$	$\tau = 4.53$ 285
$(\text{CF}_3)_4\text{Fe}(\text{CO})_4^c$	—	70.6	—	136.9	—	—	$\mathcal{J}_{\alpha-\beta} = 2.4$	70
$(\text{CF}_3)_4\text{Fe}(\text{CO})_4^c$	9.25 (ϕCF_3)	73.0	73.95 (ϕCF_3)	137.6	—	—	$\mathcal{J}_{\alpha-\beta} = 2.5$	α, β -assignments reversed in reference 173
$\text{CF}_3\text{Co}(\text{CO})_4$	-87 (CF_3COOH)	-10.4	—	—	—	—	—	237
$\text{C}_3\text{F}_5\text{Co}(\text{CO})_4$	-19.3 (CF_3COOH)	57.3	6.0 (CF_3COOH)	82.6	—	—	—	237
$\eta\text{-C}_3\text{F}_7\text{Co}(\text{CO})_4$	-25.5 (CF_3COOH)	51.1	18.4 (CF_3COOH)	95.0	2.0 (CF_3COOH)	78.6	$\mathcal{J}_{\alpha-\gamma} = 10$	α, β -assignments reversed in reference 237
$\text{C}_3\text{F}_7\text{CoCp}(\text{CO})_2\text{I}$	—	56.3	—	114.1	—	79.1	—	285
$(\text{CF}_3)_4\text{CoCp}(\text{CO})^c$	—	67.5 ^d	—	135	—	—	$\mathcal{J}_{\alpha-\beta} = 4.3$; $\tau = 4.57$ (Cp)	70
$(\text{CO})_4\text{CoCF}_2\text{CF}_2\text{Co}(\text{CO})_4$	-30.7 (ϕCF_3)	32.9	—	—	—	—	—	173
$(\text{CF}_3\text{CF}_2)_2\text{Hg}$	31.9 (CF_3COOH)	108.5	6.0 (CF_3COOH)	82.6	—	—	$\mathcal{J}_{\alpha-\beta} \sim 0$; $\mathcal{J}_{\text{Hg}-\alpha} = 770$ $\mathcal{J}_{\text{Hg}-\beta} = 71$	214
$(\text{CF}_3\text{CFH})_2\text{Hg}$	146 (CF_3COOH)	223	-0.63(CF_3COOH)	76.0	—	—	$\mathcal{J}_{\text{H}-\beta} = 13$; $\mathcal{J}_{\alpha-\beta} = 17$; $\mathcal{J}_{\text{H}-\alpha} = 48$; $\mathcal{J}_{\text{Hg}-\alpha} = 480$; $\mathcal{J}_{\text{Hg}-\beta} = 161$; $\mathcal{J}_{\text{Hg}-\text{H}} \sim 0$	$\delta_{\text{H}_2\text{O}} = -1.3$ ($\tau = 3.9$) 214
$(\text{CF}_3\text{CH}_2)_2\text{Hg}$	—	—	-28.9 (CF_3COOH)	47.7	—	—	$\mathcal{J}_{\text{H}-\text{F}} = 15$; $\mathcal{J}_{\text{Hg}-\text{F}} = 224$	$\delta_{\text{H}_2\text{O}} = 2.8$ ($\tau = 8.0$) $\mathcal{J}_{\text{Hg}-\text{H}} = 130$ 214

^a ^{19}F chemical shift (position rel. to metal).

^b Center of AB pattern. $\delta_{\text{AB}} = 15.5$ ppm, $\mathcal{J}_{\text{AB}} = 275$ cps.

^c Structure is heterocyclic ring:



^d Center of AB pattern. $\delta_{\text{AB}} = 6.26$ ppm, $\mathcal{J}_{\text{AB}} = 218$ cps.

of the B^{11} nucleus with both groups of fluorine atoms, but no F^{19} - F^{19} interaction.

Fluorine NMR has proved extremely valuable in structure determination for perfluoroalkyl derivatives of transition metals (70, 214, 285, 359). The CF_3 portion of a perfluoroalkyl group, when not directly bonded to a metal atom, has a fairly consistent chemical shift, falling in the range $\phi = 77$ -85, for both main group and transition metal derivatives. [The single exception is $(CF_3)_2CFMn(CO)_5$, which is structurally unique among the compounds reported.] This shift, together with the relative intensity of this absorption, is highly diagnostic of such a CF_3 group.

Similarly, a CF_2 group, *when not bonded directly to a transition metal*, has a fairly consistent chemical shift, falling in the range $\phi = 110$ -140. This also appears to be true for both transition metal and main group element derivatives.

It is when one considers a CF_3 or CF_2 group *directly bonded* to a transition metal with an *unfilled d orbital* that "anomalous" shifts are found. These groups appear at much lower field than the same group not so bonded, being shifted downfield an average 60-70 ppm from the "normal" region of the group. Pitcher *et al.* (285), have attributed this shift to a deshielding of the fluorines in the α position through mixing of low-lying excited states involving the fluorine atom's p_π electrons and the metal atom's empty d orbitals. These low-lying excited states in the bond between the α - CF_2 and the metal atoms gives rise to a substantial increase in the paramagnetic contribution to the magnetic screening constants of the F^{19} nuclei, with a consequent sizable downfield shift. It will be noted that interposing a carbonyl group, as in $CF_3CF_2CORe(CO)_5$, between the metal and the first CF_2 group destroys this interaction and removes the anomalous shift (Table IV).² It is also interesting to note that mercury, in $(C_2F_5)_2Hg$, often considered to be a transition metal but which has a *filled d* subshell, does not cause this downfield shift of F^{19} in the α position.

This downfield shift has served as a useful diagnostic tool in determining the structures of various hydrometallation products (284, 359). Addition of a transition metal hydride to an olefin such as $CCl_2:CF_2$ could occur so as to place either the CF_2 or the CCl_2 group in the α position. The F^{19} NMR spectrum of the product of one reaction shows the CF_2 absorption at $\phi = 45.8$, thus establishing that the CF_2 group is in the α position, viz.

² Some typical F^{19} spectra are shown in Fig. 1 of the chapter by Treichel and Stone in Volume 1 of *Advances in Organometallic Chemistry*.

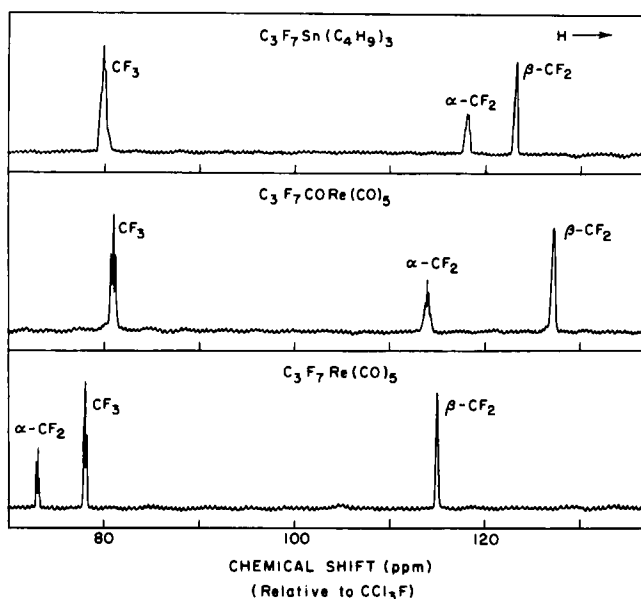
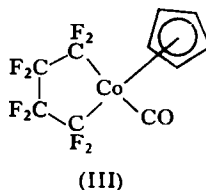
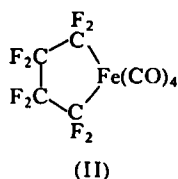


FIG. 3. Fluorine NMR spectra of perfluoroalkyl and perfluoroacyl metal derivatives (E. Pitcher, Ph.D. thesis, Harvard University, 1962, reproduced with permission).

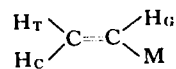
$\text{HCCl}_2\text{CF}_2\text{Mn}(\text{CO})_5$. This and related spectra are illustrated in Fig. 3. Note that the $\alpha\text{-CF}_2$ of $\text{HCFCICF}_2\text{Mn}(\text{CO})_5$ appears as an AB pattern, due to asymmetry of the HCFCI group. Later work on the addition of $\text{HMn}(\text{CO})_5$ to $\text{CF}_2=\text{CCl}_2$ (373a) has revealed a second isomer, namely $\text{HCF}_2\text{CCl}_2\text{Mn}(\text{CO})_5$.

In the case of the heterocyclic compounds (II) and (III) the observed low-



field shift permitted a decision as to which absorption went with which pair of CF_2 groups. In the case of the cobalt compound, asymmetry about the $(\text{CF}_2)_4$ ring, due to the presence of the cyclopentadienyl and CO groups on opposite sides, causes the $\alpha\text{-CF}_2$ groups to appear as an AB pattern, since

TABLE V
VINYL DERIVATIVES

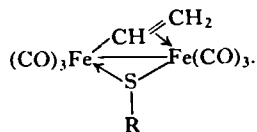


Compound	H _G		H _T		H _C		<i>J</i> _{G-T}	<i>J</i> _{C-G}	<i>J</i> _{C-T}	Remarks	References
	δ	τ	δ	τ	δ	τ					
<i>Group I</i>											
CH ₃ :CHLi	—	—	—	—	—	—	19.3	23.9	7.1	δ rel. to H _G ; H _T = 0.51; H _C = 1.19	179
<i>Group II</i>											
CH ₃ :CHMgCl/THF	—	3.32	—	3.87	—	4.43	17.6	23.0	7.5		170
CH ₃ :CHMgBr/THF	—	3.52	—	4.02	—	4.34	17.2	22.1	7.4		128
<i>Group III</i>											
(CH ₃ :CH) ₃ B	—	—	—	—	—	—	—	—	—	Multiplet, τ = 3.45; δ _{B¹¹F₃.OEt₃} = -55.2	140
(CH ₃ :CH) ₃ BMe	—	—	—	—	—	—	—	—	—	Multiplet, τ = 3.52; δ _{B¹¹F₃.OEt₃} = -64.4; τ _{CH₃} = 9.14	140
(CH ₃ :CH) ₃ BCl	—	—	—	—	—	—	—	—	—	Multiplet, τ = 3.48; δ _{B¹¹F₃.OEt₃} = -54.8	140
CH ₃ :CHBMe ₂	—	—	—	—	—	—	—	—	—	Multiplet, τ = 3.65; δ _{B¹¹F₃.OEt₃} = -74.5; τ _{CH₃} = 9.18	140
CH ₃ :CHBCl ₂	—	—	—	—	—	—	—	—	—	Multiplet, τ = 3.49; δ _{B¹¹F₃.OEt₃} = -52.4	140
CH ₃ :CHBCl ₂	—	—	—	—	—	—	—	—	—	δ _{B¹¹Cl₃} = -6.2	72
CH ₃ :CHBF ₂	—	—	—	—	—	—	—	—	—	δ _{CCl₃F} = 92.7 (neat) or 88.6 (inf diln); J _{B¹¹-F} = 67; δ _{B¹¹Cl₃} = 24.2	72, 74

$\text{CH}_2:\text{CHBF}_2\cdot 7\text{H}_2\text{O}$	—	—	—	—	—	—	—	—	—	$\delta_{\text{CCl}_4\text{F}} = 138;$ $\gamma_{\text{H}^{11}\text{-F}} = 52;$ complex vinyl peak center $\tau \sim 4$	346
$(\text{CH}_2:\text{CH})_3\text{Al}\cdot\text{OEt}_2$	-4.79 (C_6H_6)	3.7	-4.53 (C_6H_6)	3.9	-4.18 (C_6H_6)	4.3	15.3	21.4	6.3		252
$(\text{CH}_2:\text{CH})_3\text{Ga}$	—	3.414	—	3.735	—	4.127	14.92	21.16	5.03		256
$(\text{CH}_2:\text{CH})\text{Ti}(\text{ClO}_4)_3$	—	—	—	—	—	—	12.8	20.0	4.3	D_2O soln, $\gamma_{\text{Ti}^{105}\text{-O}} = 2004;$ $\gamma_{\text{Ti}^{105}\text{-C}} = 1806;$ $\gamma_{\text{Ti}^{105}\text{-T}} = 3750$ conc. dependent	220
$(\text{CH}_2:\text{CH})_3\text{TiClO}_4$	—	—	—	—	—	—	—	—	—	D_2O soln, $\gamma_{\text{Ti}^{105}\text{-G}} = 842;$ $\gamma_{\text{Ti}^{105}\text{-C}} = 805;$ $\gamma_{\text{Ti}^{105}\text{-T}} = 1618$	220
$(\text{CH}_2:\text{CH})_{3-n}\text{TiMe}_n$	—	2.47	—	3.37	—	5.87	—	—	—	1.0 M soln in benzene- d_6 at 26°C conc and solvent-dependent	220
<i>Group IV</i>											
$(\text{CH}_2:\text{CH})_4\text{Si}$	-0.26 (H_2O)	4.9	-0.65 (H_2O)	4.6	-0.64 (H_2O)	4.6	-10.7	15.3	1.0	Probably incorrect γ 's	40
$(\text{CH}_2:\text{CH})_4\text{Si}$	—	—	—	—	—	—	15.33	20.47	2.70	Both "consistent with experimental spectrum"	51
$(\text{CH}_2:\text{CH})_4\text{Si}$	—	—	—	—	—	—	14.7	19.95	4.38		
$(\text{CH}_2:\text{CH})_4\text{Si}$	—	3.89	—	3.93	—	4.23	14.6	20.4	3.6	"Best values"	171
$(\text{CH}_2:\text{CH})_3\text{Si}\phi$	—	3.73	—	3.88	—	4.23	14.7	20.4	3.7	$\tau\phi \sim 2.7$	171
$(\text{CH}_2:\text{CH})_2\text{Si}\phi_2$	—	3.56	—	3.82	—	4.24	14.7	20.4	3.6	$\tau\phi \sim 2.7$	171
$(\text{CH}_2:\text{CH})_2\text{SiMe}_2$	—	5.34	—	5.52	—	5.78	14.6	20.2	3.7	$\tau_{\text{CH}_3} = 8.68$	172
$\text{CH}_2:\text{CHSi}\phi_3$	—	3.36	—	3.78	—	4.25	14.7	20.4	3.6	$\tau\phi \sim 2.7$	171
$\text{CH}_2:\text{CHSiMe}_3$	—	5.34	—	5.58	—	5.82	14.6	20.4	3.8	$\tau_{\text{CH}_3} = 8.62$	172
$(\text{CH}_2:\text{CH})_6\text{Ge}_3$	—	3.806	—	4.042	—	4.408	13.32	20.07	2.93		52
$(\text{CH}_2:\text{CH})_4\text{Sn}$	-4.79 (C_6H_6)	3.7	-4.60 (C_6H_6)	3.9	-4.15 (C_6H_6)	4.3	13.2	20.3	3.7	$\gamma_{\text{Sn-G}} = 98.3;$ $\gamma_{\text{Sn-T}} = 183.1;$ $\gamma_{\text{Sn-C}} = 90.6$	252
$(\text{CH}_2:\text{CH})_4\text{Sn}$	-1.31 (H_2O)	3.9	-1.11 (H_2O)	4.1	-0.67 (H_2O)	4.5	16.1	20.7	2.6		40
$(\text{CH}_2:\text{CH})_4\text{Sn}$	—	—	—	—	—	—	—	—	—	Multiplet center, $\tau \approx 3.80$	140
$(\text{CH}_2:\text{CH})_2\text{SnCl}$	-1.53 (H_2O)	3.7	-1.34 (H_2O)	3.9	-1.00 (H_2O)	4.2	12.6	19.1	2.4		40
$\text{CH}_2:\text{CHSnBu}_2\text{Cl}$	-1.79 (H_2O)	3.4	-1.53 (H_2O)	3.7	-1.17 (H_2O)	4.0	15.0	21.4	2.4		40

TABLE V—continued

Compound	H _G		H _T		H _C		<i>J</i> _{G-T}	<i>J</i> _{C-G}	<i>J</i> _{C-T}	Remarks	References
	δ	τ	δ	τ	δ	τ					
(CH ₃ :CH) ₄ Pb <i>Group V</i>	-1.95 (H ₂ O)	3.3	-1.36 (H ₂ O)	3.9	-0.72 (H ₂ O)	4.5	12.1	19.6	2.0		40
(CH ₃ :CH) ₃ As	-1.30 (H ₂ O)	3.9	-0.68 (H ₂ O)	4.5	-0.44 (H ₂ O)	4.8	11.5	18.8	1.6		40
(CH ₃ :CH) ₂ AsBu	-1.48 (H ₂ O)	3.7	-0.83 (H ₂ O)	4.4	-0.61 (H ₂ O)	4.6	11.9	19.4	1.9		40
CH ₃ :CHAsBu ₂	-1.51 (H ₂ O)	3.7	-0.86 (H ₂ O)	4.4	-0.64 (H ₂ O)	4.6	11.8	19.1	1.8		40
CH ₃ :CHAsφ ₂	-1.51 (H ₂ O)	3.7	-0.65 (H ₂ O)	4.6	-0.41 (H ₂ O)	4.8	11.4	19.0	1.7		40
(CH ₃ :CH) ₃ Sb <i>Transition Metals</i>	-1.68 (H ₂ O)	3.5	-1.12 (H ₂ O)	4.1	-0.68 (H ₂ O)	4.5	12.6	19.5	2.0		40
(CH ₃ :CH) ₂ Hg	-5.87 (C ₆ H ₆)	2.6	-5.06 (C ₆ H ₆)	3.4	-4.53 (C ₆ H ₆)	3.9	13.1	21.0	3.5	<i>J</i> _{Hg-G} = 128.5; <i>J</i> _{Hg-T} = 295.5; <i>J</i> _{Hg-C} = 159.6	252
Fe ₂ (CO) ₉ (CH:CH ₂)(SCH ₃)	—	1.84	—	7.15	—	6.19	9	14	< 1	Footnote <i>a</i> . CH ₃ -trip- let-τ 7.85, 7.93, 8.38	205
Fe ₂ (CO) ₉ (CH:CH ₂)(SEt)	—	1.85	—	7.17	—	6.22	9	15	< 1	Footnote <i>a</i> . τ _{CH₃} = 7.69; τ _{CH₃} = 8.70; τ _{CH₃-CH₂} = 7	205
Fe ₂ (CO) ₉ (CH:CH ₂)(S- <i>i</i> -Pr)	—	1.65	—	7.15	—	6.22	8	14	< 1	Footnote <i>a</i> . τ _{CH} = 7.48; τ _{CH₃} = 8.68; τ _{CH-CH₃} = 7	205
Fe ₂ (CO) ₉ (CH:CH ₂)(SCH:CH ₂)	—	1.84	—	7.22	—	6.18	8	14	1	Footnote <i>a</i> . δ-CH=CH ₂ , complex peak centered at τ = 4.30	205

a Compounds of structure

Vinyl spectrum AMX, rather than ABC (see discussion).

the fluorine atoms on opposite sides of the ring have acquired slightly different chemical shifts.³

Another unusual feature of the spectra of perfluoroalkyl metal derivatives, observed in most perfluoroalkyl compounds, is the absence of any coupling between fluorines on adjacent carbon atoms. Thus in a $\text{CF}_3\text{CF}_2\text{CF}_2$ group, coupling is observed between the $\alpha\text{-CF}_2$ and CF_3 groups, but is not resolvable between the $\alpha\text{-CF}_2$ and the $\beta\text{-CF}_2$, or the $\beta\text{-CF}_2$ and CF_3 . This lack of spin-spin coupling between adjacent fluorinated groups led in one case (237) to inverted assignments of the $\alpha\text{-CF}_2$ and $\beta\text{-CF}_2$ resonances. The reviewers

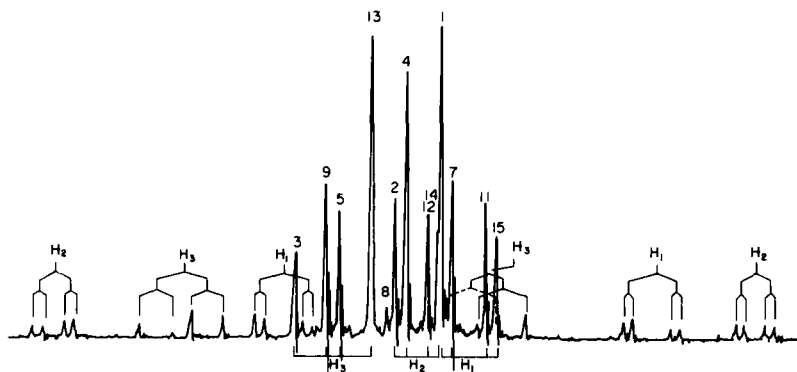


FIG. 4. Proton NMR spectrum of divinylmercury at 40 Mc/sec showing Hg^{199} satellites [Moore and Happe (252), reproduced with permission].

have taken the liberty of correcting the original assignment for inclusion in Table IV.

Vinyl Derivatives (Table V). In most vinyl metallic compounds the difference in chemical shifts of the three protons is similar in magnitude to the spin-spin coupling between these nuclei, and thus a second-order (ABC) spectrum is observed (Figs. 4 and 5). Analysis of these spectra is usually straightforward, if lengthy, and the δ and \mathcal{J} values indicated in Table V are readily calculated. However, in some cases two somewhat different solutions may appear to fit the data equally well. Such a discrepancy appears in this Table in the values given for $(\text{CH}_2:\text{CH})_4\text{Si}$ and for $(\text{CH}_2:\text{CH})_4\text{Sn}$ as

³ Varian Associates recently re-examined this compound, and were able to detect a slight splitting characteristic of an AB pattern in the β -fluorine resonance as well. (See No. 81 in the "NMR at Work" Series, Varian Assoc., Palo Alto, Calif. and Fig. 2 in the chapter by Treichel and Stone in Volume 1 of *Advances in Organometallic Chemistry*.)

reported by different investigators. The reviewers believe the best values for $(\text{CH}_2:\text{CH})_4\text{Si}$ to be those of Hobgood and Goldstein (171) but at present we are unable to comment on the values for $(\text{CH}_2:\text{CH})_4\text{Sn}$.

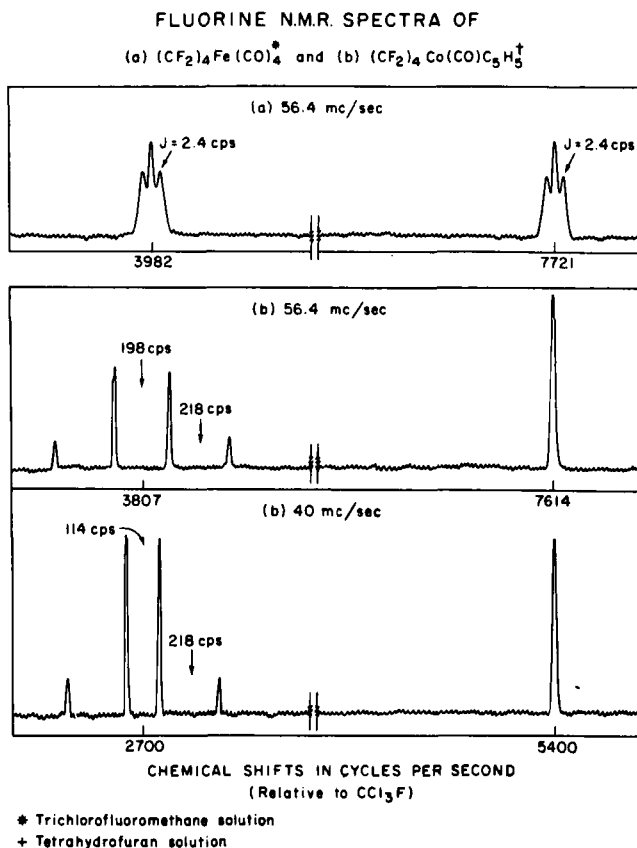


FIG. 5. Fluorine NMR spectra of heterocyclic tetradifluoromethylene metal derivatives (E. Pitcher, Ph.D. thesis, Harvard University, 1962, reproduced with permission).

The influence of the nature of the metal atom is apparent in the chemical shifts and, to a lesser degree, in the couplings within the vinyl group. The effect on shifts is greatest on the proton in the position *gem* to the metal, and least on the proton in the *cis* position. This is in accord with observations of shifts in unsaturated organic molecules in general (316).

The most outstanding example of the effect of perturbation of the

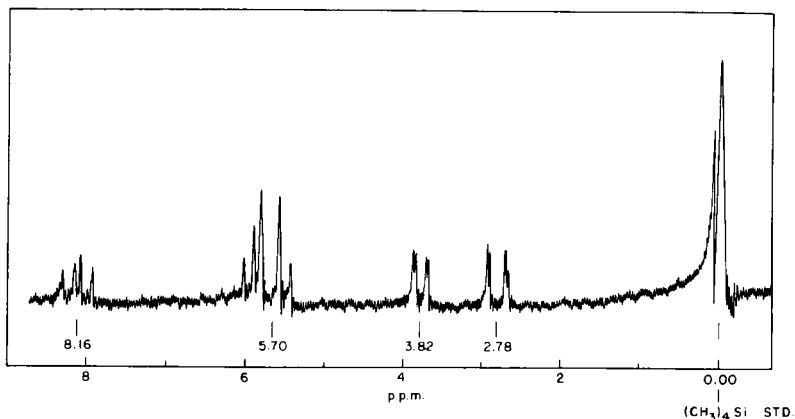
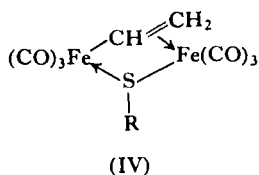


FIG. 6. Proton NMR spectrum of $(\text{CH}_2:\text{CH})_2\text{SFe}_2(\text{CO})_8$ (P. M. Treichel, Ph.D. thesis, Harvard University, 1962, reproduced with permission).


π electrons on an NMR spectrum of a vinyl group occurs in compounds of type (IV). A typical spectrum is illustrated in Fig. 6, in which R = vinyl.



The interaction of the π electrons of one vinyl group with the second iron atom has considerably increased the separation of chemical shifts, particularly of the *gem* proton, so that the spectrum has become the simple three quartets of an AMX system. The second vinyl group, not π -bonded, retains the usual vinyl multiplet pattern in the normal vinyl region. A series of similar compounds, in which the non- π -bonded vinyl group was replaced by a methyl, ethyl, or isopropyl group also exhibited the simplified AMX spectrum (205). The appearance of the methyl group as a triplet in $(\text{CH}_2:\text{CH})(\text{SCH}_3)\text{Fe}_2(\text{CO})_6$ is probably the result of contributions from several geometric isomers, and not of spin-spin coupling.

Miscellaneous Alkenyl Derivatives (Table VI). Allyllithium and allylmagnesium bromide, in tetrahydrofuran solution, appeared as AX_4 spectra,

TABLE VI
 MISCELLANEOUS ALKENYL DERIVATIVES

Compound	τ (ppm)	\mathcal{J} (cps)	Remarks	References
<i>Group I</i>				
$\text{CH}_2\text{:CHCH}_2\text{Li (AX}_4\text{)}$	—	12		179
$\text{CH}_2\text{:CHCH}_2\text{Li}$				
α	7.53	$\mathcal{J}_{\alpha\beta} = 12.0$		128
β	3.36	—		
γ	7.53	$\mathcal{J}_{\beta\gamma} = 12.0$		
<i>cis</i> -MeHC:CHLi				
α	3.70	Doublet 17.4		332
β	2.62	6.0 and 17.4	Doublet of quartets	
Me	8.12	Doublet 6.0		
<i>trans</i> -MeHC:CHLi				
α	3.30	Doublet 22.2		332
β	3.76	22.2 and 4.2	Doublet of quartets	
Me	8.32	Doublet 4.2		
 Na^+				
Me	7.87	—	Linewidth = 1–1.3 cps	
CH	4.58	—	Peaks shift to higher field at conc > 15%	236
<i>Group II</i>				
$\text{CH}_2\text{:CHCH}_2\text{MgBr (AX}_4\text{)}$				
A	2.7	12	$\delta = 0.1$ ppm (C_6H_6)	268
X	5.2	—	$\delta = 2.6$ ppm (C_6H_6)	
$\text{CH}_3\text{CH:CHCH}_2\text{MgBr}$				
α	9.29	—		271
β	4.12	—		377b
γ	5.52	—		
Me	8.45	—		
$\text{Me}_2\text{C:CHCH}_2\text{MgBr}$				
α	9.49	—		372
β	4.42	—		
Me	8.45	—		
<i>Group III</i>				
$(\text{CH}_2\text{:CMe})_3\text{Ga:NMe}_3$				
H_c	4.856	$\mathcal{J}_{bc} = 4.36$		256
H_b	4.366	$\mathcal{J}_{b-\text{Me}} = -1.67$		
Me	8.053	$\mathcal{J}_{c\text{Me}} = -1.33$		
<i>cis</i> -(MeCH:CH) $_3\text{Ga:NMe}_3$				
H_b	3.561	$\mathcal{J}_{a\text{Me}} = -1.24$		256
H_a	4.177	$\mathcal{J}_{b\text{Me}} = 6.18$		
Me	8.245	—		

Compound	τ (ppm)	\mathcal{J} (cps)	Remarks	References
<i>trans</i> -(MeCH:CH) ₃ GaNMe ₃				
a	4.213	$\mathcal{J}_{ac} = 18.22$		256
c	3.927	$\mathcal{J}_{aMe} = -1.59$		
Me	8.202	$\mathcal{J}_{cMe} = 5.61$		
<i>trans</i> -(MeCH:CH) ₃ Ga				
a	4.248	$\mathcal{J}_{aMe} = -1.59$		256
c	3.728	$\mathcal{J}_{cMe} = 5.0$		
Me	8.163	—		
<i>Group IV</i>				
<i>cis</i> -(MeCH:CH)GeMe ₃				
b	8.23	6.6		331
c	3.61	$\mathcal{J}_{cd} = 13.2$		
d	4.35	6.6		
<i>trans</i> -(MeCH:CH)GeMe ₃				
b	8.2	4.8		331
c } d }	4.1	$\mathcal{J}_{cd} = 19.2$		
<i>trans</i> -(MeCH:CH)SnMe ₃				
a	8.20	4.2 doublet	See Table I for SnMe ₃ group	331
b } c }	4.10	Complex pattern		
<i>cis</i> -(MeCH:CH)SnMe ₃				
a	8.25	6.6 and 1.0	Doublet of quartets	331
b	4.25	14.2	Doublet	
c	3.60	6.6	Sextet	
<i>cis</i> -(MeCH:CH) ₄ Sn				
a	8.19	6.6 doublet		331
b	3.38	$\mathcal{J}_{bc} = 13.2$		
c	4.40	—		
<i>trans</i> -(MeCH:CH) ₄ Sn				
a	8.12	4.2 doublet		331
b } c }	4.0	$\mathcal{J}_{bc} = 19.2$		
(σ -C ₆ H ₅) ₂ Sn	4.2	15.7, 16.1	$\delta = -4.4$ ppm (C ₆ H ₁₂)	82
(σ -C ₆ H ₅) ₂ Pb	3.8	—	$\delta = -4.8$ ppm (C ₆ H ₁₂)	82
<i>Transition Metals</i>				
[MeCD:CH ₂ Fe(CO) ₂ C _p] ⁺ BF ₄ ⁻				
Me	8.16	—		144
H ₃	6.53	—		
H ₄	6.06	—		

Compound	τ (ppm)	\mathcal{J} (cps)	Remarks	References
σ -C ₃ H ₅ W(CO) ₃ Cp				
CH ₂	7.68	8.4 doublet	Coupled to H ₂	150
H _{3,4}	5.47	Complex centers at 5.71, 5.47, 5.26		
H ₂	≈ 4	—	6 or 7 peaks	
σ -C ₃ H ₅ Mo(CO) ₃ Cp				69
CH ₂	7.73	Doublet 8.0		
H _{3,4}	6.5	Complex, 8 peaks		
H ₂	4.0	Complex, 6 peaks		
σ -C ₃ H ₅ Fe(CO) ₂ Cp				143
CH ₂	7.93	$\mathcal{J}_{\text{CH}_2-2} = 8.2$		
H _{3,4}	5.31	$\mathcal{J}_{23} = 9.2$		
H ₂	3.84	$\mathcal{J}_{24} = 17.1$		
σ -C ₄ H ₇ Fe(CO) ₂ Cp				143
Me	8.43	Doublet 5	Rel intensity 3	
CH ₂	7.88	Doublet 6	Rel intensity 2	
Olefinic	4.57	Complex, 9 peaks	Rel intensity 2	
σ -C ₅ H ₅ Fe(CO) ₂ Cp	3.4	—	$\delta = 0.6$ ppm (toluene)	283
σ -C ₅ H ₅ Cr(NO) ₂ Cp	3.3	—	$\delta = 0.5$ ppm (toluene)	283
(σ -C ₅ H ₅) ₂ Hg	4.3	—	$\delta = 1.5$ ppm (toluene)	283
(σ -C ₅ H ₅) ₂ Hg	4.5	—	$\delta = -0.7$ ppm (H ₂ O)	348
σ -C ₅ H ₅ CuPEt ₃				
C ₅ H ₅	3.8	—	$\delta = 1.0$ ppm (toluene)	283
Et	9.4	—	$\delta = 6.6$ ppm (toluene)	
<i>diiso</i> -C ₃ H ₅ Hg				255
	B 4.468	$\mathcal{J}_{\text{BC}} = 4.1$		
	C 5.193	$\mathcal{J}_{\text{CX}} = 1.4$		
	X 8.001	$\mathcal{J}_{\text{BX}} = 1.4$		
$\begin{array}{c} \text{Hg}_{(\text{Y})} \diagdown \\ \text{CH}_{3(\text{X})} \diagup \end{array} \text{C}=\text{C} \begin{array}{c} \text{H}_{(\text{C})} \diagup \\ \text{H}_{(\text{B})} \diagdown \end{array}$			$\mathcal{J}_{\text{BY}} = 256.5$ $\mathcal{J}_{\text{CY}} = 127.8$ $\mathcal{J}_{\text{XY}} = 88.2$	
<i>dicis</i> -C ₃ H ₅ Hg				255
	A 3.817	$\mathcal{J}_{\text{AB}} = 11.1$		
	B 3.068	$\mathcal{J}_{\text{AX}} = 1.3$		
	X 8.067	$\mathcal{J}_{\text{BX}} = 6.5$		
$\begin{array}{c} \text{Hg}_{(\text{Y})} \diagdown \\ \text{H}_{(\text{A})} \diagup \end{array} \text{C}=\text{C} \begin{array}{c} \text{CH}_{3(\text{X})} \diagup \\ \text{H}_{(\text{B})} \diagdown \end{array}$			$\mathcal{J}_{\text{AY}} = 134$ $\mathcal{J}_{\text{BY}} = 244$ $\mathcal{J}_{\text{XY}} = 12$	

Compound	τ (ppm)	J (cps)	Remarks	References
<i>ditrans</i> -C ₃ H ₅ Hg				
	A	3.817	$J_{AC} = 19.2$	255
	C	4.408	$J_{AX} = 1.3$	
	X	8.067	$J_{CX} = 5.0$	
			$J_{AY} = 125$	
			$J_{CY} = 140$	
	A	2.67	$J_{AB} = 0.6$	66
	B	3.60	$J_{AC} = 1.3$	
	C	2.3	$J_{BC} = 7.7$	
			$J_{AX} = 40.4$	
			$J_{BX} = 74.9$	
			$J_{CX} = 27.9$	

in contrast to the ABCX₂ spectrum of C₃H₅Mn(CO)₅ (Fig. 7). This result for the lithium and magnesium compounds is attributed to rapid equilibration in solution of the methylene and the terminal vinyl protons. Similar time-averaging exists for the σ -bonded C₅H₅ group when attached to heavy metals such as tin, lead, and mercury (see Section III).

Phenyl Derivatives (Table VII). Very few phenyl metal compounds have

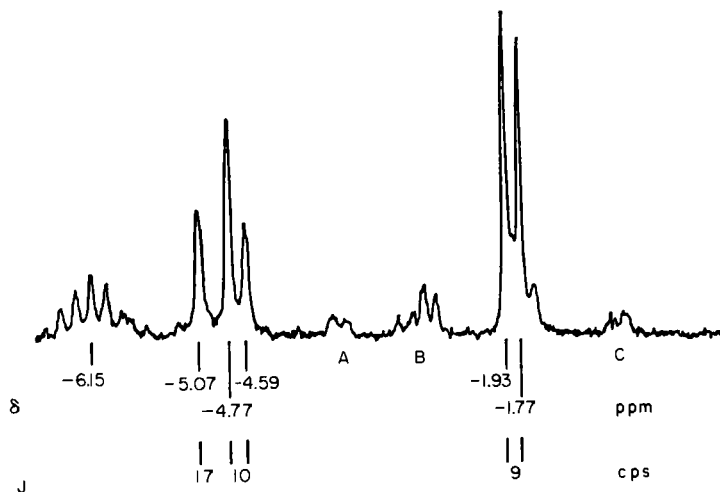


FIG. 7. Proton NMR spectrum of σ -allyl manganese pentacarbonyl [McClellan *et al.* (238) reproduced with permission].

TABLE VII

PHENYL AND PERFLUOROPHENYL DERIVATIVES

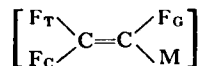
Compound	τ	Remarks	References
<i>Group 3</i>			
ϕBCl_2	—	$\delta_{\text{B}^{11}(\text{OMe})_3} = -35.9$	282
$\phi\text{B}(\text{OH})_2/\text{pyr.}$	—	$\delta_{\text{B}^{11}(\text{OMe})_3} = -15.2$	282
$\phi\text{B}(\text{OEt})_2$	—	$\delta_{\text{B}^{11}(\text{OMe})_3} = -10.4$	282
$\phi_4\text{B}^-/\text{aqueous}$	—	$\delta_{\text{B}^{11}(\text{OMe})_3} = 16.1$	282
$\phi\text{Ti}(\text{ClO}_4)_2$	—	$\text{D}_2\text{O soln, } \mathcal{J}_{\text{Ti}^{205}\text{-ortho}} = 948;$ $\mathcal{J}_{\text{Ti}^{205}\text{-meta}} = 365; \mathcal{J}_{\text{Ti}^{205}\text{-para}} = 123$	220
$\phi_2\text{TiClO}_4$	—	$\text{D}_2\text{O soln, } \mathcal{J}_{\text{Ti}^{205}\text{-ortho}} = 451;$ $\mathcal{J}_{\text{Ti}^{205}\text{-meta}} = 139; \mathcal{J}_{\text{Ti}^{205}\text{-para}} = 51$	220
$\phi_3\text{Ti}$	—	$\text{Me}_3\text{N soln, } \mathcal{J}_{\text{Ti}^{205}\text{-ortho}} = 259;$ $\mathcal{J}_{\text{Ti}^{205}\text{-meta}} = 80 \pm 5; \mathcal{J}_{\text{Ti}^{205}\text{-para}} = 35 \pm 5$	220
<i>Group 4</i>			
$\phi_3\text{SiH}$	2.64	$\text{Si—H: } \tau = 5.08; \text{CH}_3$, see Table I	366
$\phi_3\text{Si}(\text{CH:CH}_2)$	2.7	See Table V for CH:CH_2	171
$(\text{CH}_3)_2\phi_2\text{SiH}$	2.67	$\text{Si—H: } \tau = 5.57; \text{CH}_3$, see Table I	366
$\phi_2\text{Si}(\text{CH:CH}_2)_2$	2.7	See Table V for CH:CH_2	171
$(\text{CH}_3)_2\phi\text{SiH}$	2.69	$\text{Si—H: } \tau = 6.15; \text{CH}_3$, see Table I	366
$\phi\text{Si}(\text{CH:CH}_3)_3$	2.7	See Table V for CH:CH_2	171
$\phi_4\text{Si}$		See also (53)	
<i>o</i>	2.41	Shifts originally given with respect to benzene	224a
<i>m and p</i>	2.60		
$\phi_3\text{SiCl}$			
<i>o</i>	2.40		224a
<i>m and p</i>	2.64		
$\phi_2\text{SiCl}_2$			
<i>o</i>	2.10		224a
<i>m and p</i>	2.35		
ϕSiCl_3			
<i>o</i>	2.20		224a
<i>m and p</i>	2.71		
$\phi_4\text{Sn}$			
<i>o</i>	2.35		224a
<i>m and p</i>	2.57		
$\phi_3\text{SnCl}$			
<i>o</i>	2.29		224a
<i>m and p</i>	2.51		
$\phi_2\text{SnCl}_2$			
<i>o</i>	2.25		224a
<i>m and p</i>	2.42		

Compound	τ	Remarks	References
<i>Group V</i>			
$\phi_3\text{P}$	2.7		345
$\phi_3\text{As}$	2.0		345
$\phi_3\text{Sb}$	2.6		345
<i>Transition Metals</i>			
	4.15 C_8H_8	$\mathcal{J} = 14, 30, 46$, Seven bands	208
	3.07	Broad triplet	
	2.94		
	2.84		
<i>trans</i> -($\text{RuClPh}[(\text{Me}_2\text{PCH}_2)_2]_2$)	3.30	Complex absorption CDCl_3 soln	58
<i>trans</i> -($\text{RuHPh}[(\text{Me}_2\text{PCH}_2)_2]_2$)	—	$\tau_{\text{RuH}} = 23.3$ quintet $\mathcal{J} = 23.5$ Phenyl resonance not given	58
$\text{C}_6\text{F}_5\text{Mn}(\text{CO})_5$			
Ψ_o	104.3		357
Ψ_m	161.2		31a
Ψ_p	157.2		
$(\text{C}_6\text{F}_5)_2\text{TiCp}_2$			
Ψ_o	115.6		31a
Ψ_m	163.7		
Ψ_p	158.7		
$\text{C}_6\text{F}_5\text{Pb}\phi_3$			
Ψ_o	117.1		31a
Ψ_m	159.6		
Ψ_p	152.6		
$(\text{C}_6\text{F}_5)_2\text{SnMe}_2$			
Ψ_o	121.8		31a
Ψ_m	159.8		
Ψ_p	150.8		

been studied by NMR, and in no case has analysis of the proton spectrum (expected to be $\text{A}_2\text{B}_2\text{C}$) been attempted.

Perfluorovinyl Derivatives (Table VIII). Perfluorovinyl metal compounds have F^{19} spectra which are considerably simpler than the proton spectra of vinyl metals. The differences in chemical shift of the three fluorines of the perfluorovinyl group are sufficiently great that the spectra are of the simple AMX type and appear as three quartets (Fig. 8). In some instances, however,

TABLE VIII
PERFLUOROVINYL DERIVATIVES



Compound	F _T		F _C		F _G		$\mathcal{J}_{\text{CT}}^a \mathcal{J}_{\text{GT}}^a \mathcal{J}_{\text{CT}}^a$			Remarks	References
	δ	ϕ	δ	ϕ	δ	ϕ					
<i>Group III</i>											
CF ₂ :CFBCl ₂	—	71.6	—	87.9	—	184.5	7	19	114	$\delta_{\text{CCl}_2\text{F}} = 86.7 \text{ (BF}_2\text{)};$ $\mathcal{J}_{\text{C-B}^{11}\text{F}_2} = 25$	71
CF ₂ :CFBF ₂	—	72.8	—	99.8	—	206.6	18	<i>b</i>	117		71
(CF ₂ :CF) ₃ B	—	72.7	—	91.1	—	185.9	< 5	<i>b</i>	110		71
<i>Group IV</i>											
(CF ₂ :CF) ₂ Si(C ₂ H ₅) ₂	—	83.5	—	114.3	—	199.7	62	26	117		71
CF ₂ :CFSi(C ₂ H ₅) ₃	24.3 (ϕCF_3)	87.9	53.7 (ϕCF_3)	117.3	135.1 (ϕCF_3)	198.7	70	26	115		334
CF ₂ :CFSi(OC ₂ H ₅) ₃	23.5 (ϕCF_3)	87.1	50.3 (ϕCF_3)	113.9	139.8 (ϕCF_3)	203.4	59	25	117		334
(CF ₂ :CF) ₄ Ge	—	80.1	—	112.7	—	196.5	71	32	118		71
(CF ₂ :CF) ₂ Ge(CH ₃) ₂	—	86.6	—	118.6	—	195.5	72	32	118		71
CF ₂ :CFGe(C ₂ H ₅) ₃	26.4 (ϕCF_3)	90.0	58.3 (ϕCF_3)	121.9	130.8 (ϕCF_3)	194.4	79	32	115		334
(CF ₂ :CF) ₂ Sn(CH ₃) ₂	—	85.9	—	121.2	—	194.6	75	34	116	$\mathcal{J}_{\text{Sn-T}} = 29; \mathcal{J}_{\text{Sn-C}} = 25;$ $\mathcal{J}_{\text{Sn-G}^{117}} = 199; \mathcal{J}_{\text{Sn}^{119}\text{-G}} = 208^c$	71
(CF ₂ :CF) ₂ Sn(C ₆ H ₅) ₂	—	84.3	—	118.6	—	193.2	68	34	118		71
CF ₂ :CFSn(C ₄ H ₉) ₂	—	88.1	—	123.3	—	192.7	79	34	115		71
CF ₂ :CFSn(C ₂ H ₅) ₃	25.6 (ϕCF_3)	89.2	60.6 (ϕCF_3)	124.2	130.1 (ϕCF_3)	193.7	81	34	114		334
<i>Group V</i>											
(CF ₂ :CF) ₃ As	—	84.8	—	112.7	—	177.0	—	—	—		71
<i>Transition Metals</i>											
(CF ₂ :CF) ₂ Hg	—	89.9	—	124.5	—	185.0	75	37	109	$\mathcal{J}_{\text{Hg}^{199}\text{-T}} = 223;$ $\mathcal{J}_{\text{Hg}^{199}\text{-C}} = 17;$ $\mathcal{J}_{\text{Hg}^{199}\text{-G}} = 820$	71

^a Relative signs probably $\mathcal{J}_{\text{CT}}^{\pm}; \mathcal{J}_{\text{GT}}^{\pm}; \mathcal{J}_{\text{CG}}^{\pm}$ (62).

^b Not determined due to broadness of F_G and F_T peaks.

^c Sn¹¹⁷ and Sn¹¹⁹ doublets not resolved in $\mathcal{J}_{\text{Sn-T}}$ or $\mathcal{J}_{\text{Sn-C}}$.

perturbations of the absorptions were observed. It has been suggested (71) that these may arise from spin-spin interaction *between perfluorovinyl groups* on the same metal atom. This would imply that the groups may not be treated separately as giving simple AMX-type spectra. However, the necessary calculations to verify or disprove this suggestion have not yet been made.

Miscellaneous Fluoroalkenyl Derivatives (Table IX). Seyferth and Wada (333) studied a number of di(substituent)difluoroethylene compounds prepared by reaction of $(C_2H_5)_3SiCF:CF_2$ with a variety of nucleophilic reagents. Although the authors did not attempt to assign the two F^{19}

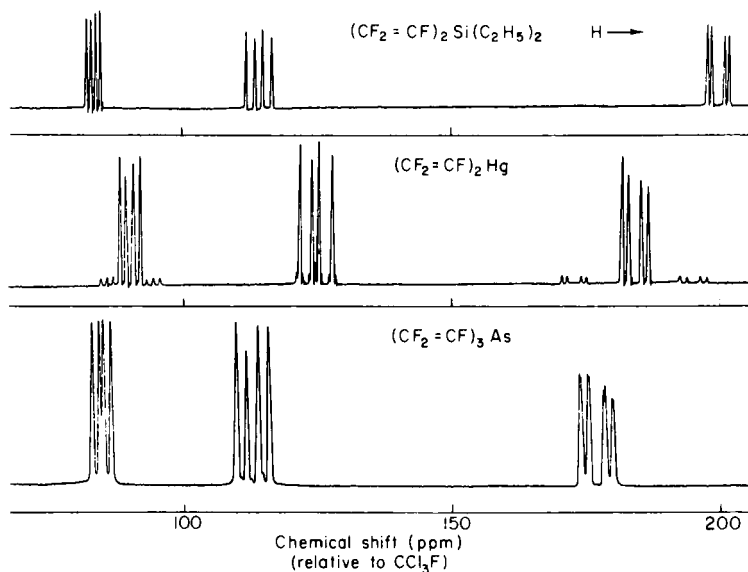


FIG. 8. Fluorine NMR spectra of some perfluorovinyl metal compounds [Coyle *et al.* (71) reproduced with permission].

resonances observed to a particular fluorine, the reviewers have taken the liberty of doing so by comparison with the shifts observed in perfluorovinylsilicon compounds.

The perfluoropropenylmanganese and -iron compounds were prepared from the appropriate sodium salt and $CF_2:CFCF_2Cl$. On the basis of the NMR spectra Pitcher and Stone (286) were able to show that the products obtained were not the anticipated perfluoroallyl derivatives, but that a rearrangement to the perfluoropropenyl group had occurred (Fig. 9). The assignment of the *trans* structure rests on a comparison of the spin-spin

TABLE IX
MISCELLANEOUS FLUOROALKENYL DERIVATIVES

Compound ^a	$\psi_{\alpha-CF}$	$\psi_{\beta-CF}$	ψ_{CF_3}	Coupling constants	Remarks	References	
<i>Group IV</i>							
Et ₃ SiCF:CF ₃	164.9	153.5	—	$\mathcal{J}_{\alpha-\beta} = 124$	<i>b</i>	333	
Et ₃ SiCF:CFC ₄ H ₉	174.0	146.8	—	$\mathcal{J}_{\alpha-\beta} = 126$; $\mathcal{J}_{\alpha-CH_3} = 23$; $\mathcal{J}_{\beta-CH_3} = 5.8$	<i>b</i>	333	
Et ₃ SiCF:CFCH ₂ CH:CH ₂	169.5	142.8	—	$\mathcal{J}_{\alpha-\beta} = 126$; $\mathcal{J}_{\alpha-CH_3} = 23$; $\mathcal{J}_{\beta-CH_3} = 6.0$	<i>b</i>	333	
Et ₃ SiCF:CFSi ϕ ₃	160.3	153.9	—	$\mathcal{J}_{\alpha-\beta} = 132$	<i>b</i>	333	
Et ₃ SiCF:CFGe ϕ ₃	158.5	154.4	—	$\mathcal{J}_{\alpha-\beta} = 144$	<i>b</i>	333	
Et ₃ SiCF:CFSC ₃ H ₇	149.4	129.5	—	$\mathcal{J}_{\alpha-\beta} = 147$	<i>b</i>	333	
<i>cis</i> -Et ₃ SiCF:CFS ϕ	120.2	96.2	—	$\mathcal{J}_{\alpha-\beta} = 20$	<i>b</i>	333	
Et ₃ SiCF:CFS ϕ	144.3	127.3	—	$\mathcal{J}_{\alpha-\beta} = 148$	<i>b</i>	333	
Et ₃ SiCF:CFOEt	194.1	118.2	—	$\mathcal{J}_{\alpha-\beta} = 122$	<i>b</i>	333	
Et ₃ SiCF:CFOCH ₂ SiMe ₃	193.2	119.3	—	$\mathcal{J}_{\alpha-\beta} = 122$	<i>b</i>	333	
<i>Transition Metals</i>							
CF ₃ CF:CFMn(CO) ₅	93.4	169.0	65.4	$\mathcal{J}_{\beta-\beta} = 135$	Originally reported rel. to CF ₃ COOH	237	
CF ₃ CF:CFMn(CO) ₅	95	165	67	$\mathcal{J}_{\alpha-\beta} = 127$; $\mathcal{J}_{\beta-CF_3} = 12$; $\mathcal{J}_{\alpha-CF_3} = 23$		286	
CF ₃ CH:C(CF ₃)Mn(CO) ₅	—	—	$\left\{ \begin{array}{l} \alpha-57.0 \\ \beta-58.8 \end{array} \right\}$	$\mathcal{J}_{\alpha-H} = 9.6$; $\mathcal{J}_{\beta-H} = 2.3$; $\mathcal{J}_{\alpha-\beta} = 2.3$	$\tau = 3.02$	359	
CF ₃ CF:CFFe(CO) ₂ Cp	86	166	66	$\mathcal{J}_{\alpha-\beta} = 131$; $\mathcal{J}_{\beta-CF_3} = 13$; $\mathcal{J}_{\alpha-CF_3} = 22$		286	
CpMn(CO) ₂ (CCF ₃) ₂	—	—	54.3	-9.3	$\tau_{Cp} = 5.2$ ϕ CF ₃ (std)	32	
(ϕ_3 P) ₂ Pt(CCF ₃) ₂	—	—	54.6	-9.0	$\mathcal{J}_{Pt^{105}-F} = 65.1$; $\mathcal{J}_{P^{31}-F} = 10.3$	ϕ CF ₃ (std)	32
(ϕ_3 As) ₂ Pt(CCF ₃) ₂	—	—	54.6	-9.0	$\mathcal{J}_{Pt^{105}-F} = 80$	ϕ CF ₃ (std)	32

^a All compounds *trans* except as noted.

^b α and β assignments made by reviewers, and refer to position relative to the Et₃Si group.

coupling constants with those of perfluoropropenyl compounds of known *cis* and *trans* configuration. Coupling constants, combined with the down-field shift expected for a fluorine on the α carbon to a transition metal (see above), also permitted distinction between the $=\text{CF}-$ resonances.

FLUORINE N.M.R. SPECTRA

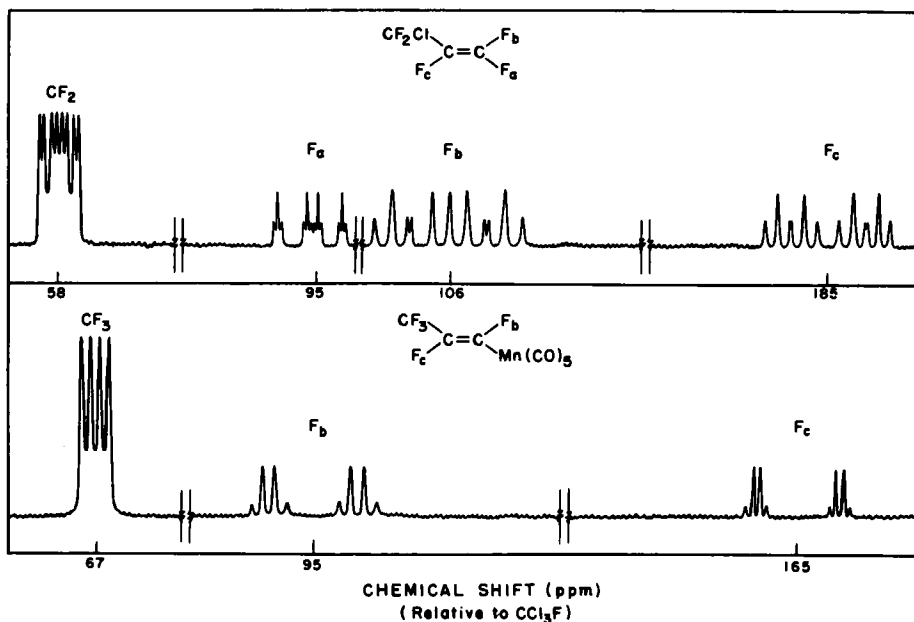


FIG. 9. Fluorine NMR spectra of perfluorallyl chloride and of perfluoropropenyl-manganese pentacarbonyl (E. Pitcher, Ph.D. thesis, Harvard University, 1962, reproduced with permission).

3. π -Bonded Olefin Complexes of Transition Metals

In general, it is observed that protons attached to an olefinic system which is coordinated to the metal in an olefin complex are shifted from a few tenths to about $3\frac{1}{2}$ ppm to higher field from their positions in the free olefin. A qualitative estimation of the source of this shift has been given (see 27), and attributed to the difference in shielding due to the π contribution in the metal-olefin bonds, contrasted with the deshielding due to the uncoordinated π electrons in the free olefin. In view of the many unknown factors, this procedure was admitted to be a vast oversimplification.

In olefin complexes bearing a positive charge, the shift to high field is attenuated, and it is often possible to observe a small net downfield shift from the position of the corresponding protons in the free olefin. These effects become rapidly attenuated as distance of proton to metal increases. Finally, the spectrum of an olefin will also show changes in proton-proton coupling constants when it has become complexed to a metal.

Any of these effects may be illustrated through a discussion of some specific examples. The olefin complexes, below, are grouped according to the number of carbon atoms of ligand participating in bonding to the metal, in the order $\pi\text{-(C}_2\text{)M}$, $\pi\text{-(C}_3\text{)M}$, $\pi\text{-(C}_4\text{)M}$, etc., so that complexes containing the most nearly comparable types of geometries and bonding situations may be grouped together. For convenience, olefins containing more than one unsaturated center coordinated with a metal but not formally conjugated to one another are regarded as chelating ligands and are grouped as multiples of the simple bonding unit they possess. This does not indicate, however, that the situation regarding magnetic resonance in such complexes is wholly comparable with the rest of the group [see, for instance, the discussion under chelating $\pi\text{-(C}_2\text{)}_n\text{M}$, below].

Within each of the Tables, some attempt has been made to list the compounds in order of increasing number of carbon atoms in the ligand. In those tables dealing with the same ligand ($\pi\text{-C}_3\text{H}_5$ or $\pi\text{-C}_5\text{H}_5$) the order is by sub-groups of the periodic classification. A formula index is given in the Appendix so that a compound known only through its empirical formula (and in which the manner of bonding to the metal is not known) may readily be located in its appropriate table.







Olefin Complexes Containing the $\pi\text{-(C}_2\text{)M}$ System. The protons in $\text{C}_2\text{H}_4\text{PtCl}_3^-$, appear at $\tau \sim 5.3$, which is higher than the resonances in the free olefin, $\tau \sim 4.0$ (291). From other shifts to higher field upon coordination to a metal, as well as the additional expected effect of the negative charge on the complex, the observed shift seems to be small. This is attributed, at least in part, to factors arising from the geometry of the attachment of ethylene to the metal, i.e., the metal-olefin axis is perpendicular to the plane of the ethylene molecule, and the dipole arising from this bond would point along the same direction as in ethylene itself [cf. Bennett, Pratt, and Wilkinson (27)]. If the electrical center of the bond is not displaced too far toward the metal atom, the shielding would still be negative and could be almost as great as in ethylene itself. On the other hand, it is not entirely unlikely that the chlorine atoms cancel, to some extent, the shift to high field which is

normally observed in other ethylene complexes. Spin-spin splitting due to Pt^{195} ($I = \frac{1}{2}$, relative abundance 34%) was observed in these complexes: $\mathcal{J}_{\text{Pt-H}} = 34$ cps. In some olefin complexes containing a metal atom of isotopes with $I = \frac{1}{2}$, proton-metal spin-spin coupling is not always observed. For instance, for the *cis*-but-2-ene complex $\text{C}_4\text{H}_8\text{PtCl}_3^-$ no satellites were observed, but the resonance at $\tau \sim 4.5$ was reported to be very broad (291). It may be that in this complex rapid chemical exchange of the olefin is occurring. The methyl resonances of the coordinated (and possibly rapidly exchanging) butene were observed at $\tau \sim 8.3$, as a broad and poorly resolved doublet; free *cis*-butene in D_2O showed this doublet at $\tau \sim 8.55$.

In solutions of some cationic olefin complexes of silver the resonances of the protons on carbon atoms directly attached to the metal were observed at $\tau \sim 3.9$, about 0.7 ppm *lower* than the region for resonance of these protons in the free olefin (291, 328). Beta protons (on carbon atoms adjacent to a π -bonded carbon) were observed at positions only about 0.1 to 0.2 ppm below the resonances of the corresponding protons in the free olefin. No spin-spin coupling satellites for any silver-olefin complexes were reported (one might expect to observe interaction of the protons with Ag^{107} and Ag^{109} , both with $I = \frac{1}{2}$, and relative abundances 51.4% and 48.6%, respectively). It must then be assumed that such interactions are either too small to observe, or that rapid intermolecular exchange of olefin has obliterated them (see the section on chemical exchange, below). In some recent work (193), the resonances of the eight protons of coordinated ethylene in $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$ were reported to occur as two *broad* absorptions at $\tau = 7.25$ and $\tau = 9.00$, showing a more normal shift to higher field. The doubling was not assigned positively as due to the effects of metal-proton spin-spin coupling (Rh^{103} , $I = \frac{1}{2}$, relative abundance 100%) since alternative explanations for this behavior were considered possible. In any case, the ring protons gave a sharp *singlet* (see below).

In recent years, a variety of complexes containing ethylene in both neutral and cationic species have been reported by E. O. Fischer and co-workers. Many of these are decomposed by water or present other obstacles to obtaining satisfactory NMR spectra. However, data for at least one of these, $(\text{C}_2\text{H}_4)_2\text{Re}(\text{CO})_4^+$, are available. This cation was reported (122) to show a single line at $\tau = 6.6$, in D_2O solution. In view of the effect of the positive charge discussed above, this represents a fairly large shift to higher field for coordinated ethylene, more characteristic of the shifts observed for olefin complexes in general. The data for the other ethylene complexes are

TABLE X
SUMMARY OF MAGNETIC RESONANCE DATA FOR COMPLEXES CONTAINING THE π -(C₂)M GROUPING, AND FOR SOME OF THE
FREE OLEFINS

Compound	δ (ppm) [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	τ	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
(C ₂ H ₄) ₂ Re(CO) ₄ ⁺	—	6.6	—	1	—	D ₂ O soln	122
(C ₂ H ₄) ₂ RhC ₅ H ₅	—	7.25	—	b	—	No coupling due to Rh ¹⁰³	193
C ₂ H ₄	—	9.00	—	b	—	($I = \frac{1}{2}$ 100% rel. abundance)	
C ₅ H ₅	—	4.92	—	—	—	reported	
C ₂ H ₄ PtCl ₃ ⁻ , K ⁺	+0.05	~5.3	—	b	—	$\delta_{\text{H}_2\text{O}} = 0$, D ₂ O soln Pt ¹⁹⁵ —H satellites $\mathcal{J}_{\text{Pt-H}} = 34$ cps	291
[C ₂ H ₄ PtCl ₂] ₂	—	—	—	—	—	Broad line resonance	297
<i>Substituted Ethylenes</i>							
C ₄ H ₈ , CH ₃ CH=CHCH ₃ (<i>cis</i>)							
	-0.72	~4.5	—	—	—	$\delta_{\text{H}_2\text{O}} = 0$, CCl ₄ soln; 40 Mc/sec	328
	+3.08	~8.3	—	—	—		
	(or +3.35)	(~8.6)				($\delta_{\text{H}_2\text{O}} = 0$, D ₂ O soln)	291
<i>cis</i> -C ₄ H ₈ ·Ag ⁺ , NO ₃ ⁻							
	-1.37	~3.8	—	—	—	$\delta_{\text{H}_2\text{O}} = 0$, D ₂ O soln	328
	+2.93	~8.1	—	—	—	40 Mc/sec	
<i>cis</i> -C ₄ H ₈ PtCl ₃ ⁻ , K ⁺							
	-0.7	~4.5	—	b	—	$\delta_{\text{H}_2\text{O}} = 0$, D ₂ O soln	291
	+3.1	~8.3	—	2	Poorly resolved		

<i>cis</i> -C ₄ H ₈ Ag ⁺ , NO ₃ ⁻							
>CH	-1.3	~3.9	—	4	—	δ _{H₂O} = 0, D ₂ O soln	291
—CH ₃	+3.0	~8.2	—	2 × 2	—		
C ₂ H ₂ ·(C ₂ O ₃)							
(C ₄ H ₂ O ₃ , maleic anhydride) }	—						
>CH	—	2.87	—	—	—	60 Mc/sec, DCCl ₃	317
	—	(or, 2.65)				40 Mc/sec, (CD ₃) ₂ CO	369
C ₄ H ₂ O ₃ ·Fe(CO) ₄							
>CH	—	5.93	—	—	—	Δτ = +3.06 ^a	317
	—	(or, 5.63)				(Δτ = +2.98) ^a	369
C ₂ H(CH ₃)(C ₂ O ₃)							
(C ₅ H ₄ O ₃ , citraconic anhydride)							
>CH	—	3.11	—	—	—	{ (CD ₃) ₂ CO, 40 Mc/sec	369
CH ₃	—	7.83	—	—	—		
C ₅ H ₄ O ₃ ·Fe(CO) ₄							
>CH	—	5.53	—	—	—	Δτ = +2.42 ^a	369
CH ₃	—	8.00	—	—	—	Δτ = +0.07 ^a	
C ₄ H ₂ (COOH) ₂ (<i>cis</i>), maleic acid							
>CH	—	3.56	—	—	—	{ 40 Mc/sec, (CD ₃) ₂ CO	369
[C ₄ H ₂ (COOH) ₂]·Fe(CO) ₄							
>CH	—	6.33	—	—	—	Δτ = +2.77 ^a	
C ₄ H ₂ (COOH) ₂ (<i>trans</i>), fumaric acid							
>CH	—	3.22	—	—	—	{ 40 Mc/sec, (CD ₃) ₂ CO	369
C ₄ H ₂ (COOH) ₂ ·Fe(CO) ₄							
>CH	—	6.58	—	—	—	Δτ = +3.36 ^a	
C ₂ H ₂ (COOH)(COOH ₂ H ₅) (<i>cis</i>)							
>CH	—	3.63	—	—	—	{ (CD ₃) ₂ CO, 40 Mc/sec	369
[C ₂ H ₂ (COOH)(COOCH ₃)]·Fe(CO) ₄							
>CH	—	6.35	—	—	—	Δτ = 2.72 ^a	

TABLE X—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
$\text{C}_2\text{H}_2(\text{COOCH}_3)_2$ (<i>cis</i>), maleic acid dimethyl ester							
>CH	—	3.52	—	—	—	60 Mc/sec, CDCl_3	317
	—	(or, 3.62)	—	—	—		
CH_3	—	6.16	—	—	—	(40 Mc/sec, $(\text{CD}_3)_2\text{CO}$)	369
$\text{C}_2\text{H}_2(\text{COOCH}_3)_2 \cdot \text{Fe}(\text{CO})_4$							
>CH	—	6.54	—	—	—	$\Delta\tau = 3.02^a$	317
	—	(or, 6.36)	—	—	—	$(\Delta\tau = 2.74)^a$	369
CH_3	—	6.24	—	—	—	$\Delta\tau = 0.08^a$ 60 Mc/sec, CCl_4 , (40 Mc/sec, CDCl_3)	
$\text{C}_2\text{H}_2(\text{COOCH}_3)_2$ (<i>trans</i>), fumaric acid, dimethyl ester							
>CH	—	3.20	—	—	—	60 Mc/sec, CDCl_3	317
	—	(or, 3.16)	—	—	—		
CH_3	—	6.24	—	—	—	(40 Mc/sec, $(\text{CD}_3)_2\text{CO}$)	369
	—	(or, 6.20)	—	—	—		
$\text{C}_2\text{H}_2(\text{COOCH}_3)_2 \cdot \text{Fe}(\text{CO})_4$						$\Delta\tau \sim 3.2^a$	317
>CH	—	~ 6.40	—	—	—	$(\Delta\tau = 3.16)^a$	369
	—	(or, 6.32)	—	—	—	$\Delta\tau = 0.16^a$	
CH_3	—	6.40	—	—	—	$(\Delta\tau = 0.04)^a$	
	—	(or, 6.24)	—	—	—	60 Mc/sec, CDCl_3 (40 Mc/sec, $(\text{CD}_3)_2\text{CO}$)	317 369

$C_2H_2(COOC_2H_5)_2$ (*trans*), fumaric acid,
diethyl ester

$\begin{array}{c} \diagup \\ \text{CH} \end{array}$	—	3.30	—	—	—
$\begin{array}{c} \diagup \\ \text{CH}_2 \end{array}$	—	5.77	—	—	—
CH_3	—	8.73	—	—	—

60 Mc/sec, $CDCl_3$

317

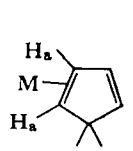
$C_2H_2(COOC_2H_5)_2 \cdot Fe(CO)_4$

$\begin{array}{c} \diagup \\ \text{CH} \end{array}$	—	6.19	—	—	—
$\begin{array}{c} \diagup \\ \text{CH}_2 \end{array}$	—	5.73	—	—	—
CH_3	—	8.64	—	—	—

$\Delta\tau = +2.89^a$

Carbocyclic Olefins

$C_5H_6Re(CO)_2C_5H_5$

	$\begin{array}{c} \diagup \\ \text{C}-\text{H} \end{array}$	—	3.1	(1)	c	—
		—	4.1	(1)	c	—
	$\begin{array}{c} \diagup \\ \text{C}-\text{H}_a \end{array}$	—	5.3	(1)	2	7
		—	5.7	(1)	c	—
	$\begin{array}{c} \diagup \\ \text{CH}_2 \end{array}$	—	6.7	(2)	c	—
	C_5H_5	—	4.4	(5)	1	—

148,

152

$C_5H_8Re(CO)_2C_5H_5$

$\begin{array}{c} \diagup \\ \text{C}-\text{H} \end{array}$	—	5.95	(2)	1	—
$(CH_2)_2$	—	7.3	(4)	c	—
CH_2	—	8.8	(2)	c	—
C_5H_5	—	3.9	(5)	1	—

148,

152


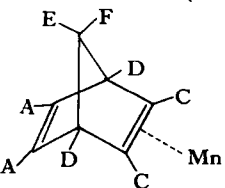
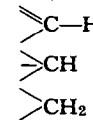
C_6H_{10} , cyclohexene

$\begin{array}{c} \diagup \\ \text{CH} \end{array}$	—0.91	~4.3	—	—	—
$\alpha\text{-CH}_2$	+2.74	~7.9	—	—	—
$\beta\text{-CH}_2$	+3.00	~8.2	—	—	—

$\delta_{H_2O} = 0$, CCl_4 soln

328

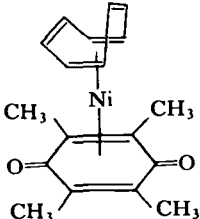
TABLE X—continued

Compound	δ (ppm) [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	τ	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References
$\text{C}_6\text{H}_{10}\text{Ag}^+$ 	-1.60	~ 3.6	—	—	—	$\delta_{\text{H}_2\text{O}} = 0$, D_2O soln	288
αCH_2	+2.60	~ 8.8	—	—	—		cf. also
βCH_2	+3.00	~ 8.2	—	—	—		328
Norbornadiene $\text{Mn}(\text{CO})_2\text{Cp}$ 	A	—	4.00	2	3	1.75	131a
C	—	6.79	2	1	—		
D	—	7.37	2	M	—		
E	—	9.18	1	2×3	1.65		
F	—	9.91	1	2×3	1.35		
<i>Chelating Diolefins</i>							
C_7H_8 , norbornadiene 	—	3.38	(4)	3	1.9	40 Mc/sec	148
>CH	—	6.50	(2)	7	~ 1.8	$21^\circ \pm 1^\circ$	cf. also
>CH_2	—	8.05	(2)	3	1.7		149 and 254

$C_7H_8Fe(CO)_3$							
$\begin{array}{c} \diagup \\ \text{C-H} \\ \diagdown \end{array}$	—	6.88	(6)	c	—	40 Mc/sec	147,
$\begin{array}{c} \diagup \\ \text{C-H} \\ \diagdown \end{array}$							148
$\begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array}$	—	8.75	(2)	3	1.4		
$[C_7H_8RhCl]_2$							
$\begin{array}{c} \diagup \\ \text{C-H} \\ \diagdown \end{array}$	—	6.12	(6)	—	—		148
$\begin{array}{c} \diagup \\ \text{C-H} \\ \diagdown \end{array}$							
$\begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array}$	—	8.80	(2)	—	—		
$C_7H_8Cr(CO)_4$							
$\begin{array}{c} \diagup \\ \text{C-H} \\ \diagdown \end{array}$	—	5.58	—	3	4.8		27
$\begin{array}{c} \diagup \\ \text{CH} \\ \diagdown \end{array}$	—	6.27	—	b	—		
$\begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array}$	—	8.70	—	3	1.4		
$C_7H_8Mo(CO)_4$							
$\begin{array}{c} \diagup \\ \text{CH} \\ \diagdown \end{array}$	—	5.03	—	3	2		207
$\begin{array}{c} \diagup \\ \text{CH} \\ \diagdown \end{array}$	—	6.18	—	—	—		
$\begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array}$	—	8.65	—	3	2		
$C_7H_8Mo(CO)_4$							
$\begin{array}{c} \diagup \\ \text{C-H} \\ \diagdown \end{array}$	—	5.15	—	3	4.4		27
$\begin{array}{c} \diagup \\ \text{CH} \\ \diagdown \end{array}$	—	6.22	—	b	—		
$\begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array}$	—	8.67	—	3	1.3		
$C_7H_8Ni(Me_4C_6O_2)$							
Me	—	7.73	6	—	—	CCl ₄ soln	327
$\begin{array}{c} \diagup \\ \text{CH}_2 \\ \diagdown \end{array}$	—	8.40	1	—	—		
$\begin{array}{c} \diagup \\ \text{CH} \\ \diagdown \end{array}$	—	6.17	1	—	—		
CH:CH	—	5.60	2	—	—		
↓							
Ni							

TABLE X—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Inten- sity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
C_8H_8 , cyclooctatetraene	—	4.3 (or, 5.48)	—	—	—	Liquid	130 29
$\text{C}_8\text{H}_8\text{Ag}^+\text{NO}_3^-^b$	—	4.3 (or, 3.5)	—	1	—	$\text{C}_6\text{H}_5\text{C}\equiv\text{N}$ soln (CH_3) ₂ SO soln	130
$\text{C}_8\text{H}_8\text{PdCl}_2$	—	4.3 (or, 4.5)	—	1	—	(CH_3) ₂ HCHO soln ($\text{C}_6\text{H}_5\text{C}\equiv\text{N}$ soln)	130
$\text{C}_8\text{H}_8\text{PtI}_2$	—	7.1	—	—	—	(CH_3) ₂ SO soln	130
$\text{C}_8\text{H}_8\text{CoC}_5\text{H}_5$	{	4.5	(4)	—	—	CDCl_3	130
C_8H_8		6.8	(4)	—	—		
C_5H_5		5.8	(5)	—	—		
$\text{C}_8\text{H}_8\text{CoC}_5\text{H}_5$	{	4.43	—	—	—	40 Mc/sec	204 (cf. also 262)
C_8H_8		6.35	—	—	—		
C_5H_5		5.33	(5)	—	—		
$\text{C}_8\text{H}_8\text{CoC}_5\text{H}_5$	{	4.56	(4)	b	—	56.45 Mc/sec, $22^\circ \pm 2^\circ$, CCl_4 soln	84
C_8H_8		6.50	(4)	b	—		
C_5H_5		5.3	(5)	1	—		
$\text{C}_8\text{H}_8(\text{CoC}_5\text{H}_5)_2$	{	6.3	(4)	—	—	Benzene	130
C_5H_5		6.1	(5)	—	—		
$[\text{C}_8\text{H}_8\text{RhCl}]_2$		4.3 5.8	— —	— —	— —		56.4 Mc/sec, CS_2 (cf. also 29)

$C_8H_8RhC_5H_5$							
C_8H_8	{ —	4.47	(4)	b	—	$\mathcal{J}_{Rh-H} = 1.4$ cps ^c	84
C_5H_5	{ —	5.94	(4)	b	—	$\mathcal{J}_{Rh-H} = 2.4$ cps	
	—	4.85	(5)	2	—	$\mathcal{J}_{Rh-C_5H_5} = 0.71$ cps CCl_4 soln, $22^\circ \pm 2^\circ C$ 56.45 Mc/sec	
C_8H_8CoCp							
$H_{3,4,7,8}$	—	4.56	1	—	Broad	CCl_4 soln	87
$H_{1,2,5,6}$	—	6.50	1	—	Broad		
C_8H_8RhCp							
$H_{3,4,7,8}$	—	4.47	—	—	Broad	CCl_4 soln	87
$H_{1,2,5,6}$	—	5.94	—	—	—	$\mathcal{J}_{Rh^{103}-H} = 2$ cps	
$C_8H_8[RhCp]_2$							
	—	5.29	1	—	—	$\mathcal{J}_{Rh^{103}-H} = 0.75$ cps	33a
	—	5.27	1	—	—		
$C_8H_8Ni[Me_4C_6O_2]$							
Me	—	7.88	3	—	—		327
Bound olefinic	—	6.13	1	—	—		
Free olefinic	—	3.98	1	—	—		
$C_8H_8NiC_{10}H_{12}O_2$							
							
C_8H_8	{ —	4.03	(1)	—	—		326
CH_3	{ —	6.18	(1)	—	—		
	—	7.92	(3)	—	—		
$C_8H_{10}Ni[Me_4C_6O_2]$							
Me	—	8.07, 7.97	6	—	—		327
CH_2	—	7.58	2	—	—		
Bound olefin	—	6.34	2	—	—		
Free olefin	—	4.20	1	—	—		

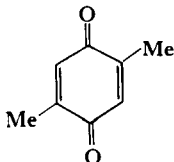
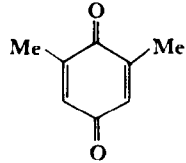
$[\text{C}_8\text{H}_{12}\text{RhCl}]_2$							
$\begin{array}{c} \diagup \\ \text{CH} \end{array}$	—	5.75	(~4)	—	—		148
$\begin{array}{c} \diagdown \\ \text{CH}_2 \end{array}$	—	7.83	(~8)	4	—		
$\text{C}_8\text{H}_{12}\text{CoC}_5\text{H}_5$							
$(\begin{array}{c} \diagup \\ \text{CH} \end{array})_4$	—	6.63	(4)	—	—	60 Mc/sec, CS_2 soln	86
$(\begin{array}{c} \diagdown \\ \text{CH}_2 \end{array})_4$	{ —	7.68	(4)	—	—		
	—	8.38	(4)	—	—		
C_5H_5	—	5.55	(5)	—	—		
$\text{C}_8\text{H}_{12}\text{Mo}(\text{CO})_4$							
$\begin{array}{c} \diagup \\ \text{CH} \end{array}$	—	5.41	—	—	—	CCl_4 soln	28
$\begin{array}{c} \diagdown \\ \text{CH}_2 \end{array}$	—	7.57	—	—	—		
$\text{C}_8\text{H}_{12}\text{Ni}[\text{Me}_4\text{C}_6\text{O}_2]$							
$\text{H}_{1,8}$	—	8.45	3	M	—		
Me	—	7.85	3	—	—	DCCl_3 soln	327
CH_2	—	7.65	2	—	—		
Bound olefin	—	6.32	1	—	—		
$\text{C}_8\text{H}_{12}\text{Ni}[\text{Me}_3\text{C}_6\text{HO}_2]$							
Me	{ —	7.89	3	—	—	CHCl_3 soln	327
	—	7.84	6	—	—		
CH_2	—	7.58	8	—	—		
Bound olefin	—	6.26	4	—	—		
CH(quinone)	—	4.10	1	—	—		
$\text{C}_8\text{H}_{12}\text{Ni},$ 							
Me	—	7.90	6	—	—	CHCl_3 soln	327
CH_2	—	7.52	8	—	—		
Bound olefin	—	6.25	4	—	—		
CH(quinone)	—	3.80	2	—	—		

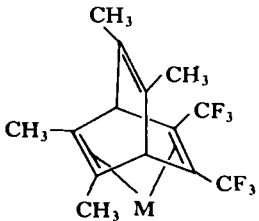
TABLE X—continued

Compound	δ (ppm) [$\delta_{(\text{CH}_4), \text{SI}} = 10$]	τ	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References
$\text{C}_8\text{H}_8\text{ONi}[\text{Me}_4\text{C}_6\text{O}_2]$	—						
Me	—	8.09	—	—	—		327
	—	8.04	—	—	—		
	—	8.00	12	—	—		
	—	7.87	—	—	—		
	—	7.75	—	—	—		
	—	7.04	1	—	—		
CH_2	—	6.72	1	—	—		
Bound olefin	—	6.23	2	—	—		
	—	5.82	2	—	—		
Free olefin	—	4.06	2	—	—		
$\text{C}_8\text{H}_{12}\text{Ni}$							
							
Me	—	7.91	6	—	—		327
CH_2	—	7.57	8	—	—		
Bound olefin	—	6.29	4	—	—		
CH(quinone)	—	3.76	2	—	—		



Me	—	7.95	12	—	—	CDCl ₃ soln	327
CH ₂	—	8.03, 7.85	4	—	—		
CH	—	7.79	4	—	—		
Bound olefin	—	6.59	1	—	—		
	—	6.29	1	—	—		
	—	5.92	1	—	—		
	—	5.74	1	—	—		
[Duroquinone] ₂ Ni	—	8.40	—	—	—	CH ₂ Cl ₂ soln	327
Bis(trifluoromethyl)tetramethylbicyclo- [2,2,2] octatriene, C ₁₄ H ₁₄ F ₆	—	—	—	—	—	δ _F ¹⁹ { CF ₃ = -335 cps (CFC ₂) ₂ (int) = 0	190
C ₁₄ H ₁₄ F ₆ · Fe(CO) ₃							
<div style="display: flex; justify-content: space-around; align-items: center;"> <div> <p>(type H—H)</p> </div> </div>							
>C—H	—	5.90	(1)	—	—	δ _F ¹⁹ { CF ₃ = -335 cps (CFC ₂) ₂ (int) = 0	190
CH ₃	—	8.37	(6)	—	—	ca. 85% of reaction product	

TABLE X—continued

Compound	δ (ppm) [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	τ	Relative Inten- sity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
$\text{C}_{14}\text{H}_{14}\text{F}_6 \cdot \text{Fe}(\text{CO})_3$							
 (type H—F)							
CH	—	6.25	(1)	—	—	$\delta_{\text{F}}^{19} \left\{ \begin{array}{l} \text{CF}_3 = -540 \text{ cps} \\ (\text{CFCl}_2)_2(\text{int}) = 0 \end{array} \right.$ <i>ca.</i> 15% of reaction product	190
CH_3	—	8.25	(3)	—	—		
CH_3	—	8.32	(3)	—	—		
$\text{C}_{14}\text{H}_{14}\text{F}_6 \cdot \text{CoC}_5\text{H}_5$							
(type (H—F))							
CH	—	6.32	(2)	—	—	$\delta_{\text{F}}^{19} \left\{ \begin{array}{l} \text{CF}_3 = -595 \text{ cps} \\ (\text{CFCl}_2)_2(\text{int}) = 0 \end{array} \right.$ No isomer of type (H—H) was observed	190
CH_3	—	8.42	(6)	—	—		
CH_3	—	8.45	(6)	—	—		
C_5H_5	—	5.37	(5)	—	—		

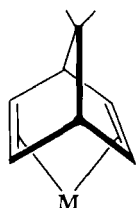
^a $\Delta\tau$ = resonance in complex — resonance in free ligand.

^b When freshly prepared shows two resonances (equal intensity) $\tau = 2.74, 5.83$, which in time become one resonance at $\tau = 2.9$, see (19).

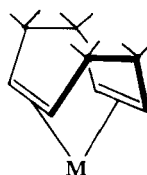
^c Rh^{103} coupling observed only under proton-proton double irradiation.

awaited with interest; it will then be possible to reach some conclusion about the comparatively small shift to high field of the protons in the ethylene complexes of platinum and silver. These and other magnetic resonance data for related compounds are presented in the first part of Table X.

In the latter part of Table X, magnetic resonance data are listed for some chelating diolefins containing the $\pi-(C_2)M$ bonding unit. These include the complexes of bicycloheptadiene (C_7H_8) (V), cycloocta-1,5-diene (C_8H_{12}) (VI), and a selected number of cyclooctatetraene complexes in

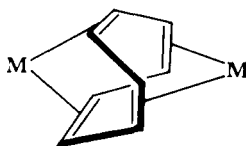
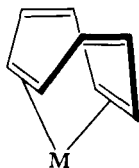


$\pi-(C_7H_8)M$
(V)



$\pi-(C_8H_{12})M$
(VI)

which the diene system functions as a chelating diolefin (VII). [This olefin is also known to bond to transition metals, particularly to iron, as a $\pi-(C_4)M$



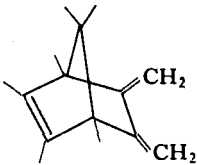




(VII)

system, see below.] An important difference between complexes containing chelating olefins as opposed to those containing two or more unconnected $\pi-(C_2)M$ systems is that in the former, because of the geometry of the carbon framework in the ligand, the metal-olefin bond axis may not be perpendicular to the plane of the olefin group, as it can be in the latter. This may lead to different shieldings of protons in these complexes.

The complexes of 5,6-dimethylenebicyclo[2.2.1]heptene-2, a chelating triolefin, contain both $\pi-(C_2)M$ and $\pi-(C_4)M$ systems, and are separately listed in Table XI.

TABLE XI

PROTON RESONANCES IN 5,6-DIMETHYLENEBICYCLO[2.2.1]HEPTENE-2, AND ITS π COMPLEXES WITH THE CARBONYLS OF Cr, Mo, AND W^a

				
	(2) ^b	(4) ^b	(2) ^b	(2) ^b
C ₉ H ₁₀	τ	τ [M] ^c \mathcal{J} (cps)	τ [M] \mathcal{J} (cps)	τ
Free olefin	4.08	5.03 [2] —	6.76 — —	8.33
C ₉ H ₁₀ Cr(CO) ₃	6.87	6.77 [2] 13	7.92 [4?] 11	8.87
C ₉ H ₁₀ Mo(CO) ₃	6.57	6.65 [2] 18	8.03 [4] —	8.38
C ₉ H ₁₀ W(CO) ₃	5.77	5.89 [2] 15	7.70 [4?] —	8.32

^a Taken from King and Stone (207).

^b Relative intensity.

^c [M], multiplicity.

If one of the protons of ethylene is replaced by a different chemical group, the remaining protons become magnetically nonequivalent, forming an ABC or ABX system of nuclei. This same feature is preserved in the metal complexes of such olefins, and the resonance data for a number of these, and for the free ligands (if available) are presented in Table XII. The series of complexes (C₂H₃)Fe₂(CO)₆SR (205), are unusual in that they contain both a π -bonded and a σ -bonded vinyl metallic group. These have been discussed in the section on vinyl metal derivatives above, and listed in Table XII as well. The values of the *gem*, *cis*, and *trans* proton-proton coupling constants in the metal complexes of the vinyl group are not significantly different from those observed in free vinyl derivatives, and it is therefore a reasonably simple matter to analyze the spectra and obtain a satisfactory assignment for the proton resonances. Except for the unusual low-field chemical shift of the proton in the vinyl complexes of iron carbonyl mentioned above, the protons of complexed vinyl groups are not markedly different in their relative positions from that in the free ligand; the entire pattern is shifted, on the average, by about 3 ppm to higher field in the complexes.

TABLE XII

SUMMARY OF MAGNETIC RESONANCE DATA FOR UNSYMMETRICALLY SUBSTITUTED ETHYLENE COMPLEXES CONTAINING AN AX OR AN ABX π -(C₂)M SYSTEM, AND FOR SOME OF THE FREE LIGANDS

Compound	τ				$J_{\text{H-H}}$ (cps)				Remarks	References
	H ₍₂₎	H ₍₃₎	H ₍₁₎	Other	1-2	1-3	2-3	Other		
<div> ϕ <div> <div>H₍₃₎</div> <div>C=C</div> <div>H₍₂₎</div> <div>COOH</div> </div> </div>										
Free ligand	2.25	3.46	—	—	—	—	17.0	—		369
Fe(CO) ₄ complex	4.87	5.68	—	—	—	—	11.0	—		
$\Delta\tau$	2.62	2.22	—	—	—	—	—	—		
<div> ϕ <div> <div>H₍₃₎</div> <div>C=C</div> <div>H₍₂₎</div> <div>CHO</div> </div> </div>										
				<u>CHO</u>				$J_{(\text{H})_2-\text{CHO}}$		369
Free ligand	2.37	3.23	—	0.25	—	—	15.8	7.9		
Fe(CO) ₄ complex	4.83	5.25	—	0.78	—	—	12.5	4.0		
$\Delta\tau$	2.46	2.02	—	0.53	—	—	—	—		

TABLE XII—continued

Compound	τ				$\mathcal{J}_{\text{H-H}}$ (cps)				Remarks	References
	H ₍₂₎	H ₍₃₎	H ₍₁₎	Other	1-2	1-3	2-3	Other		

$$\begin{array}{c}
 \text{H}_{(1)} \quad \text{H}_{(3)} \\
 \diagdown \quad \diagup \\
 \text{C} = \text{C} \\
 \diagup \quad \diagdown \\
 \text{H}_{(2)} \quad \text{X}
 \end{array}$$

X = COOH

Free ligand ~4.05 ~3.50 ~3.80 — 0.8 9.7 15.4 —

Fe(CO)₄ complex 7.20 7.11 6.58 — 1.3 8.1 10.6 —

$\Delta\tau$ 3.15 3.61 2.78 — — — — —

cf. Castellano and Waugh (50)

369

X = COOCH₃

Free ligand ~4.18 ~3.90 ~3.60 — 1.6 10.2 16.4 —

Fe(CO)₄ complex 7.22 7.09 6.57 — 1.1 8.0 10.8 —

$\Delta\tau$ 3.04 3.19 2.97 — — — — —

cf. Castellano and Waugh (50)

369

X = CONH₂

Free ligand ~4.36 ~3.80 ~3.58 — — — — —

Fe(CO)₄ complex 7.30 7.06 6.36 — 1.9 7.6 11.4 —

$\Delta\tau$ 2.94 3.26 2.78 — — — — —

369

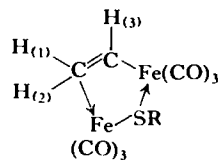
X = CHO

Free ligand $\overbrace{3.40, 3.75}$ — 0.42 — — — —

Fe(CO)₄ complex 6.97 7.01 6.05 0.55 2.5 8(?) 12.5 —

$\Delta\tau$ $\overbrace{2.30, 3.57}$ — 0.13 — — — —

369



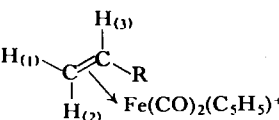
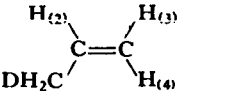
(CO) ₃				<u>R</u>						
R = CH ₃	7.15	1.84	6.19	7.85 7.93 8.38	—	9	14	—	Two geometrical isomers detected	205
R = C ₂ H ₅	7.17	1.85	6.22	7.68 8.70	—	9	15	$\mathcal{J}_{\text{CH}_2\text{CH}_3} = 7$		205
R = (CH=CH ₂)	7.22	1.84	6.18	4.30	~1	9	15			205
R = CH(CH ₃) ₂	7.15	1.65	6.22	7.48 8.68 <u>C₆H₄</u>	—	8	14	$\mathcal{J}_{\text{CH}(\text{CH}_3)_2} = 7$		205
C ₈ H ₆ S · Fe(CO) ₃	—	1.10	4.60	3.05	—	9	—		CS ₂ soln, 60 Mc/sec	205
				<u>R and C₅H₅</u>						
R = CH ₃	6.05	5.00	6.53	8.14 and 4.65	—	8	17	$\mathcal{J}_{\text{CH}_3-\text{H}(3)} = 6$		143
R = CH ₂ D	6.05	5.00	6.55	8.13 and 4.38	—	8	16			143
R = C ₂ H ₅	6.05	5.10	6.57	7.95 and 4.36	—	8	15	—		143
R = C ₂ H ₄ D	6.08	5.14	6.59	7.70 and 4.41	—	8	15	—		143

TABLE XII—continued

68

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
$[\text{C}_3\text{H}_5\text{DMo}(\text{CO})_3\text{Cp}]\text{PF}_6$						
	7.97	2	6	$\mathcal{J}_{23} = 8.0$	SO ₂ soln	69
	6.44	2	3	$\mathcal{J}_{24} = 16.0$		
	4.72	1	6	—		
	4.05	5	1	—		
$[\text{C}_3\text{H}_6\text{Mo}(\text{CO})_3\text{Cp}]\text{PF}_6$						
CH ₃	7.99	3	2	$\mathcal{J}_{\text{MeH}_2} \approx 6.8$	SO ₂ soln	69
H _{3,4}	6.44	2	3	$\mathcal{J}_{23} \approx 8.0$		
H ₂	4.98	1	7	$\mathcal{J}_{24} \approx 16.0$		
Cp	4.05	5	1	—		
$[\text{C}_3\text{H}_6\text{W}(\text{CO})_3\text{Cp}]\text{PF}_6$						
Me	7.78	3	2	$\mathcal{J}_{\text{MeH}_2} = 6.3$		150
H _{3,4}	6.71	2	7	—		
H ₂	5.64	1	11	—		
Cp	4.01	5	1	—		
$[\text{C}_3\text{H}_5\text{DFe}(\text{CO})_2\text{Cp}]\text{BF}_4$						
Me	8.16	3	1	—	SO ₂ soln	144
H ₃	6.53	1	1	—		
H ₄	6.06	1	1	—		
Cp	4.40	5	1	—		
$[\text{C}_3\text{H}_5\text{DFe}(\text{CO})_2\text{Cp}]\text{ClO}_4$						
CH ₂ D	8.13	2	8	$\mathcal{J}_{23} = 8$	SO ₂ soln	143
H ₃	6.55	1	2	$\mathcal{J}_{24} = 16$		
H ₄	6.05	1	2	—		
H ₂	5.00	1	11	—		
Cp	4.38	5	1	—		

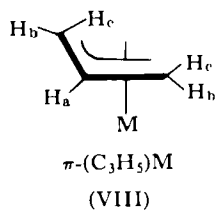
[C ₄ H ₇ DFe(CO) ₂ Cp]ClO ₄						
<div><div><div><div>H₍₂₎</div><div>H₍₃₎</div></div><div>C=C</div><div><div>CH₃CHD</div><div>H₍₄₎</div></div></div><div>C₂H₄D</div></div>	7.70	4	—	—	Complex band, spread 60 cps	143
H ₃	6.59	1	2	$\mathcal{J}_{23} = 8$	SO ₂ soln	
H ₄	6.08	1	2	$\mathcal{J}_{24} = 15$		
H ₂	5.14	1	8	—		
Cp	4.41	5	1	—		
[C ₄ H ₈ Fe(CO) ₂ Cp]ClO ₄						
Et	7.95	5	27	—	Spread 100 cps SO ₂ soln	143
H ₃	6.57	1	2	$\mathcal{J}_{23} = 8$		
H ₄	6.05	1	2	$\mathcal{J}_{24} = 16$		
H ₂	5.10	1	10	—		
Cp	4.36	5	1	—		
[(MeCHCH ₂)Mo(CO) ₃ Cp]PF ₆						
<div><div><div><div>H₍₂₎</div><div>H₍₃₎</div></div><div>C=C</div><div><div>Me</div><div>H₍₄₎</div></div></div><div><div>Me</div><div>H_{3,4}</div><div>H₂</div></div></div>	7.99	3	2	$\mathcal{J}_{24} = 16.0$	H ₄ <i>trans</i> to H ₂	69
	6.44	2	3	$\mathcal{J}_{23} = 8.0$	Liq. SO ₂	
	4.05	1	7	$\mathcal{J}_{\text{Me}-2} = 6.8$		
(CH ₂ DCHCH ₂)Mo(CO) ₃ Cp]PF ₆						
CH ₂ D	7.97	2	6	$\mathcal{J}_{23} = 8.0$	Liq. SO ₂	69
CH	4.72	1	6	$\mathcal{J}_{24} = 16.0$		
CH ₂	6.44	2	3	—		
[(MeCHCH ₂)W(CO) ₃ Cp]PF ₆						
Me	7.78	3	2	$\mathcal{J}_{\text{MeH}_2} = 6.3$	—	150
H _{3,4}	6.71	2	7	—		
H ₂	5.64	1	11	—		
[MeCHCH ₂ Fe(CO) ₂ Cp]BF ₄						
Me	8.16	3	1	—	Liq. SO ₂	144
H ₃	6.53	1	1	—		
H ₄	6.06	1	1	—		

TABLE XII—continued

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
[MeCHCH₂Fe(CO)₂Cp]ClO₄						
Me	8.14	3	2	$\mathcal{J}_{\text{MeH}_2} = 6$	Liq. SO ₂	143
H ₂	5.00	1	7	$\mathcal{J}_{23} = 8$		
H ₃	6.53	1	2	—		
H ₄	6.05	1	2	$\mathcal{J}_{24} = 17$		
[DCH₂CHCH₂Fe(CO)₂Cp]ClO₄						
CH ₂ D	8.13	2	8	—	Liq. SO ₂	143
H ₃	6.55	1	2	$\mathcal{J}_{23} = 8$		
H ₄	6.05	1	2	—		
H ₂	5.00	1	11	$\mathcal{J}_{24} = 16$		
[CH₃CH₂CHCH₂Fe(CO)₂Cp]ClO₄						
CH ₃ CH ₂	7.95	5	27	—	Spread 100 cps	143
H ₃	6.57	1	2	—	Liq. SO ₂	
H ₄	6.05	1	2	$\mathcal{J}_{23} = 8$		
H ₂	5.10	1	10	$\mathcal{J}_{24} = 16$		
[C₃H₆Fe(CO)₂Cp]ClO₄						
Me	8.14	3	2	$\mathcal{J}_{\text{MeH}_2} = 6$	SO ₂ soln	143
H ₃	6.53	1	2	$\mathcal{J}_{23} = 8$		
H ₄	6.05	1	2	—		
H ₂	5.00	1	7	$\mathcal{J}_{24} = 17$		
Cp	4.68	5	—	—		
[CH₃CHDCHCH₂Fe(CO)₂Cp]ClO₄						
CHDCH ₃	7.70	4	C	—	Spread 100 cps	143
H ₃	6.59	1	2	$\mathcal{J}_{23} = 8$	Liq. SO ₂	
H ₄	6.08	1	2	—		
H ₂	5.14	1	8	$\mathcal{J}_{24} = 16$		

It has recently been reported that acrylonitrile, $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$, may be bonded to a metal through the lone pair on nitrogen, as in acrylonitrile-tungsten pentacarbonyl (230, 352; see also 311). This is of interest in view of earlier reports of complexes in which this ligand is believed to be attached to the metal through the olefinic system (see Massey, 230, or Tate *et al.* 352, for references to previous work). Proton magnetic resonance spectra can be used to differentiate between the two types of complex: The spectrum of the former is remarkably similar to that obtained for free acrylonitrile, while in the latter type, the resonances show a much greater perturbation of the olefinic system arising from π coordination to the metal.

Derivatives Containing the π -(C_3)M System. The parent radical for this type of olefin complex is the π - C_3H_5 group, for which three major resonances are observed in the intensity ratio 1:2:2, i.e. for the protons labeled H_a , H_b ,



and H_c , respectively in (VIII). NMR data for a number of complexes containing the π - C_3H_5 group are given in Table XIII. The proton H_a is generally observed to be the least shielded of the three; its position will vary over the range $3 \leq \tau \leq 6$ (see Table XIII). Under high resolution, the resonance for H_a appears as a pattern of overlapping triplets due to splitting by the two equivalent pairs of protons, H_b and H_c .⁴ The coupling constants $\mathcal{J}_{\text{H}_a-\text{H}_b}$ and $\mathcal{J}_{\text{H}_a-\text{H}_c}$ are observed to have values over the range 3 to 10 and 8 to 14 cps, respectively, similar to those found for *cis*- and *trans*-coupling constants of protons in an olefinic system (see metal vinyl compounds, above). The resonances of H_b and H_c appear at higher fields, well separated from each other and from H_a , at τ values of 5.6 to 6.6, and 7 to 8, respectively. Under high resolution, the resonances for H_b and H_c appear as doublets, from the coupling of each to H_a . The coupling of H_b to H_c (*gem* coupling) is usually too small to be observed, i.e. less than about 1 cps. When the allylic system is part of a ring, i.e. protons H_c are replaced by carbon-carbon bonds as in cyclopentenyl (C_5H_7) (IX) or cyclohexenyl (C_6H_9) (X) groups, the resonance

⁴ The reader is referred to the chapter by Green and Nagy in Volume 2 (p. 332) of *Advances in Organometallic Chemistry* for further discussion of this subject.

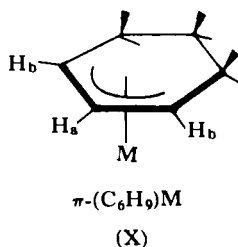
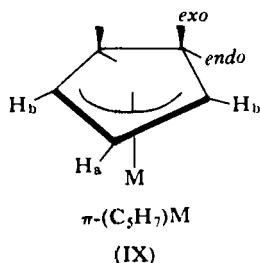
TABLE XIII
SUMMARY OF MAGNETIC RESONANCE DATA FOR DERIVATIVES CONTAINING THE π -C₃H₅ GROUP

Compound	H _a	τ^a H _b	H _c	γ_{ac} (cps)	γ_{ab} (cps)	Remarks	References
[C ₃ H ₅ NiBr] ₂	5.7	7.7	8.8	13.3	7.0	C ₆ H ₆ soln, 60 Mc/sec	44
[C ₃ H ₅ PdCl] ₂	4.55	5.93	7.00	12.1	6.9	CHCl ₃ , 60 Mc/sec	336, 337
[C ₃ H ₅ PdCl] ₂	(0.88)	(2.26)	(3.3)	12.8	6.4	$\delta_{C_4H_4}$ (ext.) = 0	89
	~3.51	~4.89	~5.9			CHCl ₃ , 60 Mc/sec and 15.1 Mc/sec	
[C ₃ H ₅ PdCl] ₂	3.89	5.32	6.30	12	3	CDCl ₃	238
[C ₃ H ₅ PdBr] ₂	6.15	7.0	8.2	12.2	6.9	C ₆ H ₆ , 60 Mc/sec	44
[C ₃ H ₅ PdI] ₂	4.60	5.65	6.95	11.8	6.3	CHCl ₃ , 40 Mc/sec	337
C ₃ H ₅ NiClP ϕ ₃	(0.97)	(3.12)	(3.95)	—	—	CDCl ₃ , $\delta_{C_4H_4}$ (ext.) = 0;	169
	~3.60	~5.75	~6.58			(C ₆ H ₅) ₃ P, $\tau \approx 1.6$	
C ₃ H ₅ Co(CO) ₃	5.09	6.94	7.86	10	6	56.4 Mc/sec	238, 167
C ₃ H ₅ Mn(CO) ₄	5.30	7.31	8.28	14	10	56.4 Mc/sec	238, 183
C ₃ H ₅ NiC ₅ H ₅	6.30	6.91	8.13	11	3	$\tau_{C_3H_5} = 4.21$	238
C ₃ H ₅ PdC ₅ H ₅	4.32	5.63	6.81	10	5	$\tau_{C_3H_5} = 3.5$	238
C ₃ H ₅ PdC ₅ H ₅	5.43	6.60	7.90	10.4	5.7	$\tau_{C_3H_5} = 4.14$	337
C ₃ H ₅ PtC ₅ H ₅ ^b	~6.4	~6.43	~7.97	~8	~4	$\tau_{C_3H_5} = 4.25$	337
C ₃ H ₅ Fe(CO)C ₆ H ₅	5.84	7.33	9.32	11	8	C ₆ H ₆ soln, 60 Mc/sec	143
						$\tau_{C_3H_5} = 5.94$	

$C_3H_5Mo(CO)_2C_5H_5$	6.72	7.40	9.13	12	7.6	$C_6H_6 + CS_2$ soln, 60 Mc/sec	69
$[C_3H_5PdCl]_2$	4.57	5.93	6.91	12.0	6.9	$CHCl_3$, 60 Mc/sec	306
$C_3H_5Pd(acac)$	4.53	6.26	7.20	11.8	6.5	$Me(acac)$, $\tau = 8.12$	306
						$CH(acac)$, $\tau = 4.83$	
						CCl_4 , 60 Mc/sec	
$C_3H_5CoIC_5H_5$	(1.35)	(1.87)	(3.30)	—	—	$CDCl_3$, 60 Mc/sec	166
	4.98	4.50	5.93	—	—	$\delta_{C_6H_6}$ (ext.) = 0.0	
						$\tau_{CP} = 3.93$ (1.2)	
$C_3H_5CoBrC_5H_5$	(2.00)	(1.17)	(3.67)	—	—	$CDCl_3$, 60 Mc/sec	166
	4.63	3.80	6.30	—	—	$\delta_{C_6H_6}$ (ext.) = 0.0	
						$\tau_{CP} = 4.06$ (1.33)	
$C_3H_5W(CO)_2C_5H_5$	6.75	7.52	8.88	13.8	6.8	C_6H_6 , 60 Mc/sec	150
						$\tau_{CP} = 5.37$	

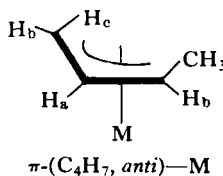
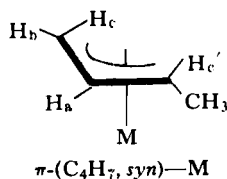
^a Chemical shift values reported in units of *tau*; where other units were reported, these are listed in parentheses, and approximate corresponding tau values listed (determined according to conversion table given earlier).

^b Spin-spin coupling due to Pt^{195} isotope are reported as follows: J (cps) $Pt-H_c = 54$, $Pt-H_b = 29$, $Pt-C_5H_5 = 10.5$ (cf. Smith, 343).



formerly attributed to H_c is no longer observed and resonances at slightly higher fields, $\tau = 8.5$ to 9.2 , are seen for the methylene groups on carbon atoms not associated with the olefinic system [see Shaw and Sheppard (337), Fischer and Werner (126), and data presented in Table XIV].

π -Allyl complexes are also known in which either H_b or H_c , or both of these, are replaced by a methyl or other organic group (Table IX). When one methyl group is substituted on the terminal carbon of the simple π -allyl framework, two isomeric forms are possible for the ligand in the complex: a *syn* and an *anti* form (XI). Such a methyl group is split into a doublet by



(XI)

H_b or $H_{c'}$, $\mathcal{J} = 6$ cps and appears at $\tau = 7.7$ – 8.2 , the highest field position of the proton resonances of the ligand. Assignment of all the resonances has been made (253) (Table XIV). The chemical shifts and coupling constants for protons H_a , H_b , and H_c are similar to those given above for the unsubstituted allyl group.

The general pattern of resonances in this type of (nonclassical) π -allyl complex is such that it is possible to differentiate it from rapidly tautomerizing species such as the Grignard reagent containing this group (269). For the case of π -allylpalladium derivatives, a nonclassical resonance pattern (A_2B_2C) was observed in solvents like $CDCl_3$, but it was found that with solvents of greater donor power, like dimethyl sulfoxide, the resonance pattern of the allylic group was changed to that of a rapidly tautomerizing σ -bonded group (AX_4) (61).⁵

⁵ See Sections II, B, 2 and III.

TABLE XIV

SUMMARY OF MAGNETIC RESONANCE DATA FOR MISCELLANEOUS OLEFIN COMPLEXES CONTAINING THE π -(C₃)M SYSTEM

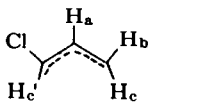
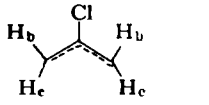
Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
α -Cl—C ₃ H ₄ Co(CO) ₃ , 	H _b — H _c — H _a —	5.32 6.65 7.62 4.01	(1) (1) (1) (1)	2 2 2 m	8 8 11 —	Relative position of Cl and H _{c'} not specified.	238
β -Cl—C ₃ H ₄ Co(CO) ₃ 	H _b — H _c —	6.17 7.08	(2) (2)	1 1	$\mathcal{J}_{bc} \sim 0$ —		238
C ₄ H ₇ Co(CO) ₃ (<i>syn</i>) H _a H _b H _c H _{c'} CH ₃	1.89 3.73 4.65 3.49 5.03	~ 4.5 ~ 6.4 ~ 7.3 ~ 6.1 ~ 7.7	— — — — —	— — — — —	$\mathcal{J}_{ab} = 6.3$ $\mathcal{J}_{ac, ac'} = 10.5$ $\mathcal{J}_{c'CH_3} = 6.5$ $\mathcal{J}_{bc, bc'} < 0.2$ —	$\delta_{\text{C}_4\text{H}_8} (\text{ext.}) = 0$; 40 Mc/sec	252 238
C ₄ H ₇ Co(CO) ₃ (<i>anti</i>) H _a H _b H _{b'} H _c CH ₃	1.65 3.35 2.38 3.80 5.45	~ 4.3 ~ 6.0 ~ 5.0 ~ 6.4 ~ 8.1	— — — — —	— — — — —	$\mathcal{J}_{ab} = 7.1$ $\mathcal{J}_{ac} = 12.3$ $\mathcal{J}_{ab'} = 6.8$ $\mathcal{J}_{bb'} = 1.6$ $\mathcal{J}_{b'-CH_3} = 7.0$	$\delta_{\text{C}_4\text{H}_8} (\text{ext.}) = 0$; 40 Mc/sec	252 238

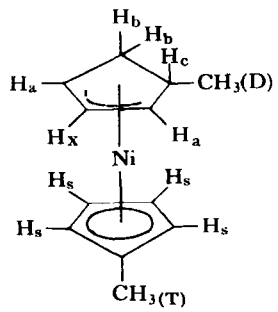
TABLE XIV—continued

Compound	δ (ppm)	τ [$\delta(\text{CH}_3)_4\text{Si} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
[C ₄ H ₇ PdCl] ₂ ^a							
H _a	0.97	~3.6	—	—	$\mathcal{J}_{ac} = 6.3$	$\delta_{\text{C}_4\text{H}_7}$ (ext.) = 0; CDCl ₃ soln	89
H _b	3.49	~6.1	—	—	$\mathcal{J}_{ab'} = 12.0$		
H _{b'}	2.44	~5.1	—	—	$\mathcal{J}_{ab} = 11.5$		
H _c	2.39	~5.0	—	—	$\mathcal{J}_{c'\text{CH}_3} = 6.0$		
CH ₃	5.0	~7.6	—	—			
C ₄ H ₇ Fe(CO) ₃ Cl							
H _a	—	5.08	(1)	c	—	60 Mc/sec, CCl ₄	178
H _b	—	5.83	(2)	2	—	Assignment consistent with <i>anti</i>	
H _c	—	7.10	—	2	—	isomer; no coupling constants	
H _{b'}	—	5.83	(1)	2	—	reported	
CH ₃	—	7.93	(3)	2	—		
C ₄ H ₇ Fe(CO) ₃ I							
H _b	—	5.97	(2)	1	$\mathcal{J}_{bc} \sim 0$	60 Mc/sec, CHCl ₃	287
H _c	—	6.28	(2)	1	—	Assignments consistent with	
CH ₃	—	7.98	(3)	1	—	2-methyl- π -allyl group	
[C ₄ H ₇ PdCl] ₂							
H _b	—	6.17	(2)	1	$\mathcal{J}_{bc} \sim 0$	Assignment consistent with 2-methyl- π -allyl group	337
H _c	—	7.17	(2)	1	—		
CH ₃	—	7.90	(3)	1	—		
[(C ₄ H ₆ Cl)PdCl] ₂							
H _a	—	~4.55	—	—	$\mathcal{J}_{ab} = 6.9$	60 Mc/sec, CHCl ₃	336
H _b	—	~5.98	—	—	$\mathcal{J}_{ac} = 12.0$	H _{b'} (or H _{c'}) and CH ₂ Cl, not	
H _c	—	~6.97	—	—	—	given	

[(C ₄ H ₆ OCH ₃)PdCl] ₂							
H _a	—	~4.5	—	—	$\mathcal{J}_{ab} = 6.9$	60 Mc/sec, CHCl ₃	336
H _b	—	~6.0	—	—	$\mathcal{J}_{ac} = 12.3$	H _{b'} (or H _{c'}) and OCH ₃ not	
H _c	—	~7.03	—	—	—	given	
C ₅ H ₉ Fe(CO) ₃ ⁺ , BF ₄ ⁻ 1,1 dimethyl- π -allyl							
H _a ^b	—	4.35	(1)	4	—	60 Mc/sec, in liq. SO ₂ ;	104
H _b ^b	—	5.72	(1)	4	—	no coupling constants reported,	
H _c ^b	—	6.60	(1)	4	—	but spectrum was very nearly	
CH ₃ ^b	—	{ 7.64	(3)	1	—	first order	
		8.04	(3)	1	—		
C ₅ H ₇ NiC ₅ H ₅							
H _a	—	5.93	—	c	—		99
H _b	—	8.51	—	c	—		
H _c	—	9.24	—	c	—		
(CH ₂) ₂	—	—	—	—	—		
C ₅ H ₅	—	4.78	—	1	—		
C ₅ H ₇ NiC ₅ H ₅							
H _a	—	4.87	(1)	—	—		124, 125
H _b	—	6.04	(2)	—	—		180
(CH ₂) ₂	—	8.93	(4)	—	—		
C ₅ H ₅	—	4.72	(5)	—	—		
C ₅ H ₇ Cr(CO) ₂ (C ₅ H ₅)							
H _a	—	4.9	(1)	—	—	60 Mc/sec	132
H _b	—	6.0	(2)	—	—		
(CH ₂) ₂	—	8.9	(4)	—	—		
C ₅ H ₅	—	4.7	(5)	—	—		

TABLE XIV—continued

78

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	J (cps)	Remarks	References
$(\text{C}_5\text{H}_6\text{CH}_3)\text{Ni}(\text{C}_5\text{H}_4\text{CH}_3)$							
							
$\text{H}_\text{S} + \text{H}_\text{x}$	—	4.90	(5)	—	—		125
H_A	—	6.19	(2)	—	—		
H_T	—	7.99	(3)	—	—		
H_C	—	8.32	(1)	—	—		
H_D	—	8.65	(3)	—	—		
H_B	—	8.86	(2)	—	—		
$[\text{C}_6\text{H}_9\text{PdCl}]_2 \pi\text{-cyclohexenyl}$							
H_a	—	~ 3.3	(1)	—	—	40 Mc/sec C_6H_6	337
H_b	—	5.20	(2)	—	—		180
$(\text{CH}_2)_2$	—	8.60	(4)	—	—		
CH_2	—	9.11	(2)	—	—		

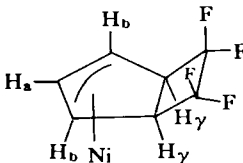
C₆H₉PdC₅H₅						40 Mc/sec, CCl ₄ ; also measured in C ₆ H ₆ for which slightly different values obtained	337 125
H _a	—	3.52	(1)	—	—		
H _b	—	5.28	(2)	—	—		
(CH ₂) ₃	—	8.59	(6)	—	—		
C ₅ H ₅	—	4.35	(5)	—	—		
C₆H₉Mo(CO)₂C₆H₇						Resonances unassigned; this compound can also exist in isomeric form, as (C ₆ H ₈) ₂ Mo(CO) ₂ . See Table XV	132
—	—	4.0	(1)	—	—		
—	—	5.35	(3)	—	—		
—	—	7.05	(2)	—	—		
—	—	8.2	(6)	—	—		
—	—	9.1	(4)	—	—		
C₆F₉Fe(CO)₃							
F _a	8064 cps	—	—	—	—	56.45 Mc/sec, NH ₂ CHO soln δ _{C₆H₃F₃} (int) = 0	272
F _b	7718 cps	—	—	2	J _{ab} = 50		
F ⁻	3910	—	—	—	—		
(CF ₂) ₃	1935	—	—	2	45		
	2167	—	—	2	45		
	3103	—	—	3	217		
C₇H₅F₄NiC₅H₅							
							
H _a	—	4.48	(1)	—	—	60 Mc/sec, CCl ₃ soln Fluorine resonance: A B quartet complete analysis given	235
H _b	—	6.07	(2)	c	—		
H _γ	—	7.33	(2)	c	—		
C ₅ H ₅	—	4.75	(5)	—	—		

TABLE XIV—continued

Compound	δ (ppm)	τ [$\delta(\text{CH}_3)_4\text{Si} = 10$]	Relative Inten- sity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
$\text{C}_7\text{H}_5\text{F}_3\text{ClNiC}_5\text{H}_5$							
H_a	—	4.53	(1)	—	—	60 Mc/sec, CCl_3F soln	235
H_b	—	6.07	(2)	c	—	Fluorine resonance: ABB' pattern	
H_γ	—	7.22	(2)	c	—		
C_5H_5	—	4.78	(5)	—	—		
$[\text{C}_6\text{H}_9\text{OPdCl}]_2$							
	—	6.29	—	—	—	For phosphine and amine	277
	—	7.50	—	—	—	substituted complexes, cf. (172)	(cf. also
	—	7.55	—	—	—	Hobgood <i>et al.</i> (172)	278)
	—	7.84	—	—	—		
	—	8.61	—	—	—		
$\text{C}_{11}\text{H}_{11}\text{O}_3\text{NiC}_5\text{H}_5$							
$\text{R} = \text{CH}_3\text{C}-$							

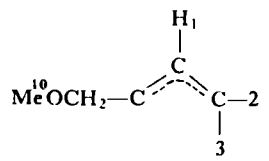
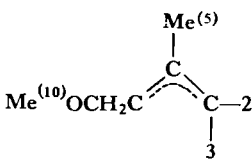
H ₀	—	3.45	(2)	3	—		98
(CH ₃) ₂ + 2H _t	—	6.3	(8)	c	—		
H _a	—	7.82	(1)	3	—		
C ₅ H ₅	—	4.76	(5)	—	—		
C ₁₃ H ₁₇ NiC ₅ H ₅ (see text)							
		{ 7.66	(3)	—	—		193
		{ 8.46	(3)	—	—		
4CH ₃	—	{ 9.05	(3)	—	—		
		{ 9.09	(3)	—	—		
C ₅ H ₅	—	4.95	(5)	1	—		
		{ 3.79	(1)	1	—		
		{ 3.83	(1)	2	$\gamma = 10$		
5H	—	{ 5.75	(1)	2	$\gamma = 10$		
		{ 7.25	(1)	1	—		
		{ 7.45	(1)	1	—		
[MeOCH ₂ C ₃ H ₄ PdCl] ₂							
							
H ₁	—	4.50	—	—	$\gamma_{12} = 6.9$	CDCl ₃ , 60 Mc/sec	306
H ₂	—	6.00	—	—	$\gamma_{13} = 12.2$		
H ₃	—	7.03	—	—	—		
H ₁₀	—	6.58	—	—	—		
[MeOCH ₂ C ₃ H ₄ PdBr] ₂							
H ₁	—	4.50	—	—	$\gamma_{12} = 6.8$	CHCl ₃ , 60 Mc/sec	306
H ₂	—	5.93	—	—	$\gamma_{13} = 11.9$		
H ₃	—	6.99	—	—	—		
H ₁₀	—	6.58	—	—	—		

TABLE XIV—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
[ClCH₂C₃H₄PdCl]₂							
H ₁	—	4.55	—	—	$\mathcal{J}_{12} = 6.9$	CHCl ₃ , 60 Mc/sec	306
H ₂	—	5.98	—	—	$\mathcal{J}_{13} = 12.0$		
H ₃	—	6.97	—	—	—		
[But-2-enyl PdCl]₂							
H ₁	—	4.73	—	—	$\mathcal{J}_{12} = 6.5$	CHCl ₃ , 60 Mc/sec	306
H ₂	—	6.10	—	—	$\mathcal{J}_{13} = 12.1$		
H ₃	—	7.18	—	—	—		
H ₇	—	8.65	—	—	—		
[MeOCH₂CHCMeCH₂PdCl]₂							
							
H ₂	—	6.16	—	—	—	CHCl ₃ , 60 Mc/sec	306
H ₃	—	7.12	—	—	—		
H ₄	—	6.37	—	—	—		
H ₅	—	7.83	—	—	—		
H ₁₀	—	6.59	—	—	—		
CH ₂	—	6.37	—	—	—		

[MeOCH ₂ C ₄ H ₆ PdBr] ₂						CHCl ₃ , 60 Mc/sec	306
H ₂	—	6.11	—	—	—		
H ₃	—	7.12	—	—	—		
H ₄	—	6.30	—	—	—		
H ₅	—	7.92	—	—	—		
H ₁₀	—	6.59	—	—	—		
CH ₂	—	6.30	—	—	—		
[MeOCH ₂ C ₄ H ₆ PdI] ₂						CDCl ₃ , 60 Mc/sec H ₄ and CH ₂ not given	306
H ₂	—	5.96	—	—	—		
H ₃	—	7.17	—	—	—		
H ₅	—	8.07	—	—	—		
H ₁₀	—	6.60	—	—	—		
[MeOCH ₂ C ₄ H ₆ PdSCN] ₂						CDCl ₃ , 60 Mc/sec	306
H ₂	—	6.22	—	—	—		
H ₃	—	7.24	—	—	—		
H ₄	—	6.37	—	—	—		
H ₅	—	7.98	—	—	—		
H ₁₀	—	6.62	—	—	—		
CH ₂	—	6.37	—	—	—		
MeOCH ₂ C ₄ H ₆ Pd(acac)						CCl ₄ , 60 Mc/sec H ₄ not given	306
H ₂	—	6.48	—	—	—		
H ₃	—	7.33	—	—	—		
H ₅	—	7.82	—	—	—		
H ₁₀	—	6.64	—	—	—		
(acac) Me	—	8.14	—	—	—		
(acac) CH	—	4.84	—	—	—		
MeOCH ₂ C ₄ H ₆ PdCp						CCl ₄ , 60 Mc/sec	306
H ₅	—	8.03	—	—	—		
H ₁₀	—	6.70	—	—	—		
Cp	—	4.45	—	—	—		

TABLE XIV—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References
[MeOCMe ₂ C ₃ H ₄ PdCl] ₂							
H ₁	—	4.53	—	—	$\gamma_{12} = 6.8$	CHCl ₃ , 60 Mc/sec	306
H ₂	—	6.00	—	—	$\gamma_{13} = 11.6$		
H ₃	—	7.02	—	—	$\gamma_{14} = 11.4$		
H ₄	—	6.25	—	—	—		
H ₉	—	8.6	—	—	—		
H ₁₀	—	6.70	—	—	—		
[MeOCMe ₂ C ₃ H ₄ PdI] ₂							
H ₁	—	4.64	—	—	$\gamma_{12} = 7.0$	CHCl ₃ , 60 Mc/sec	306
H ₂	—	5.87	—	—	$\gamma_{13} = 12.2$		
H ₃	—	7.10	—	—	$\gamma_{14} = 12.2$		
H ₄	—	5.96	—	—	—		
H ₉	—	8.50, 8.55	—	—	—		
H ₁₀	—	6.71	—	—	—		
MeOCMe ₂ C ₃ H ₄ PdCp							
H ₁	—	5.17	—	—	$\gamma_{12} = 6.4$	CCl ₄ , 60 Mc/sec	306
H ₂	—	6.55	—	—	$\gamma_{13} = 10.5$		
H ₃	—	7.88	—	—	—		
H ₄	—	6.9	—	—	—		
H ₉	—	8.66, 8.75	—	—	—		
H ₁₀	—	6.85	—	—	—		
Cp	—	4.38	—	—	—		
[MeOCH ₂ C ₅ H ₈ PdCl] ₂							
H ₅	—	7.86	—	—	—	CDCl ₃ , 60 Mc/sec	306
H ₈	—	8.60	—	—	—		
H ₁₀	—	6.79	—	—	—		

[MeOCH ₂ C ₅ H ₈ PdBr] ₂						CDCl ₃ , 60 Mc/sec	306
H ₅	—	7.92	—	—	—		
H ₈	—	8.46	—	—	—		
H ₁₀	—	6.81	—	—	—		
[MeOMe ₂ CC ₅ H ₈ PdCl] ₂						CHCl ₃ , 60 Mc/sec	306
H ₁	—	4.93	—	—	<i>J</i> ₁₄ = 11.9		
H ₄	—	6.18	—	—	—		
H _{6, 7}	—	8.61 or 8.77	—	—	—		
H ₉	—	8.61	—	—	—		
H ₁₀	—	6.70	—	—	—		
[MeOCMe ₂ C ₅ H ₈ PdI] ₂						CHCl ₃ , 60 Mc/sec Other peaks not assigned but due to one Me of type 6, one of type 7, and two of type 9 (split by rotational isomerism)	306
H ₁	—	4.89	—	—	—		
H ₄	—	5.93	—	—	—		
H ₁₀	—	6.70	—	—	—		
		8.13, 8.48,					
		8.54					
		8.67					
MeOCMe ₂ C ₅ H ₈ PdCp						CHCl ₃ , 60 Mc/sec	306
H ₁	—	5.22	—	—	<i>J</i> ₁₄ = 10.4		
H ₄	—	6.62	—	—	—		
H ₉	—	8.65, 8.75	—	—	—		
H ₁₀	—	6.85	—	—	—		
Cp	—	4.50	—	—	—		
MeOCMe ₂ C ₅ H ₈ Pd(acac)						CCl ₄ , 60 Mc/sec	306
H ₂	—	6.62	—	—	—		
H ₃	—	7.44	—	—	—		
H ₅	—	7.69	—	—	—		
(acac)Me	—	8.18	—	—	—		
(acac)CH	—	4.90	—	—	—		

TABLE XIV—*continued*

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Inten- sity	Multi- plicity	J (cps)	Remarks	References
[MeOCMe ₂ C ₄ H ₆ PdCl] ₂							
H ₂	—	6.28	—	—	—	CHCl ₃ , 60 Mc/sec	306
H ₃	—	7.21	—	—	—		
H ₄	—	6.55	—	—	—		
H ₅	—	7.76	—	—	—		
H ₉	—	8.53, 8.62	—	—	—		
H ₁₀	—	6.67	—	—	—		
MeOCMe ₂ C ₄ H ₆ Pd(acac)							
H ₂	—	6.53	—	—	—	CCl ₄ , 60 Mc/sec	306
H ₃	—	7.36	—	—	—		
H ₄	—	6.93	—	—	—		
H ₅	—	7.69	—	—	—		
H ₉	—	8.53, 8.63	—	—	—		
H ₁₀	—	6.71	—	—	—		
(acac)Me	—	8.12	—	—	—		
(acac)CH	—	4.82	—	—	—		
MeOCMe ₂ C ₄ H ₆ PdCp							
H ₅	—	7.93	—	—	—	CCl ₄ , 60 Mc/sec	306
H ₉	—	8.63	—	—	—		
H ₁₀	—	6.76	—	—	—		
Cp	—	4.40	—	—	—		

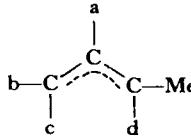
$C_4H_7Pd(acac)$								
H_2	—	6.48	—	—	—		CCl_4 , 60 Mc/sec	306
H_3	—	7.34	—	—	—			
H_5	—	7.79	—	—	—			
(acac)Me	—	8.13	—	—	—			
(acac)CH	—	4.83	—	—	—			
$[C_4H_7PdCl]_2$								
H_2	—	6.15	—	—	—		$CHCl_3$, 60 Mc/sec	306
H_3	—	7.12	—	—	—			
H_5	—	7.86	—	—	—			
$Me_2C:CC_4H_6PdCp$								
H_2	—	6.76	—	—	—		CCl_4 , 60 Mc/sec	306
H_3	—	7.84	—	—	—			
H_5	—	7.96	—	—	—			
Cp	—	4.51	—	—	—			
$[MeCOC_4H_6PdCl]_2$								
	—	6.29	—	—	—			279
	—	7.50	—	—	—			
	—	7.55	—	—	—			
	—	7.84	—	—	—			
	—	8.61	—	—	—			
$MeC_3H_4Co(CO)_3$								
	a	1.90	≈ 4.53	—	—	$J_{ac} = 10.5$	$\delta_{C_6H_6} = 0$	30
	b	3.72	≈ 6.35	—	—	$J_{ab} = 6.3$		
	c	4.65	≈ 7.28	—	—	$J_{ad} = 10.5$		
	d	3.48	≈ 6.11	—	—	$J_{bc} < 0.2$		
	Me	5.03	≈ 7.66	—	—	$J_{bd} < 0.2$		
						$J_{dMe} = 6.5$		

TABLE XIV—continued

Compound		δ (ppm)	τ [$\delta_{(CH_3)_4Si} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
Me'C₃H₄Co(CO)₃								
	a	1.55	≈ 4.18	—	—	$\gamma_{ab} = 7.1$	$\delta_{C_6H_6} = 0$	30
	b	3.35	≈ 6.98	—	—	$\gamma_{ac} = 12.3$		
	c	3.80	≈ 6.43	—	—	$\gamma_{ad} = 6.8$		
	d	2.38	≈ 5.01	—	—	$\gamma_{bc} = 0.6$		
	Me'	5.45	≈ 8.08	—	—	$\gamma_{bd} = 1.6$		
						$\gamma_{dMe} = 7.0$		
Me'C₄H₅Co(CO)₃								
	a	1.90	≈ 4.53	—	—	$\gamma_{ab} = 6.4$	$\delta_{C_6H_6} = 0$	30
	b	3.57	≈ 6.20	—	—	$\gamma_{ac} = 11.2$		
	c	4.13	≈ 6.76	—	—	$\gamma_{bc} = 1.2$		
	Me	4.88	≈ 7.51	—	—	—		
	Me'	5.35	≈ 8.98	—	—	—		
MeMe'C₄H₅Co(CO)₃								
	b	3.50	≈ 6.13	—	—	$\gamma_{bc} = 0.8$	$\delta_{C_6H_6} = 0$	30
	c	3.99	≈ 6.62	—	—	—		
	Me''	4.67	≈ 7.30	—	—	—		
	Me	4.82	≈ 7.45	—	—	—		
	Me'	5.32	≈ 7.95	—	—	—		

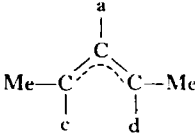
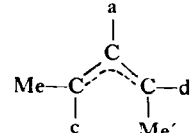
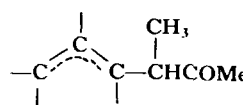
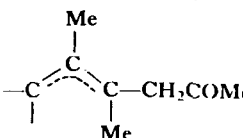
EtC₃H₄Co(CO)₃							
a	1.90	≈ 4.53	—	—	$\mathcal{J}_{ab}=6.2$	$\delta_{C_4H_6}=0$	30
b	3.70	≈ 6.33	—	—	$\mathcal{J}_{ac}=10.4$		
c	4.69	≈ 7.32	—	—	$\mathcal{J}_{ad}=10.0$		
d	3.62	≈ 6.25	—	—	$\mathcal{J}_{bc}<0.2$		
CH ₂	4.90	≈ 7.53	—	—	$\mathcal{J}_{bd}<0.2$		
CH ₃	5.50	≈ 8.13	—	—	Et 7.1		
					$\mathcal{J}_{dCH_2}=6.3$		
Et'C₃H₄Co(CO)₃							
a	1.73	≈ 4.36	—	—	$\mathcal{J}_{ab}=6.4$	$\mathcal{J}_{CH_2CH_3}$ (not obs.)	30
b	3.39	≈ 6.02	—	—	$\mathcal{J}_{ac}=10.9$		
c	3.90	≈ 6.53	—	—	$\mathcal{J}_{ad}=7.0$	$\delta_{C_4H_6}=0$	
d	2.45	≈ 5.08	—	—	$\mathcal{J}_{bc}=0.8$		
CH ₂	5.17	≈ 7.80	—	—	$\mathcal{J}_{bd}=1.6$		
CH ₃	5.62	≈ 8.25	—	—	$\mathcal{J}_{dCH_2}=6.3$		
C₅H₉Co(CO)₃							
							
a	2.67	≈ 5.30	—	—	$\mathcal{J}_{ac}=9.8$	$\delta_{C_4H_6}=0$	30
c	3.72	≈ 6.35	—	—	$\mathcal{J}_{ad}=9.8$		
d	3.72	≈ 6.35	—	—	$\mathcal{J}_{dMe}=6.5$		
Me	5.09	≈ 7.72	—	—	—		
C₅H₉Co(CO)₃							
							
a	1.85	≈ 4.48	—	—	$\mathcal{J}_{ac}=11.3$	$\delta_{C_4H_6}=0$	30
c	3.75	≈ 6.38	—	—	$\mathcal{J}_{ad}=7.2$		
d	2.77	≈ 5.40	—	—	$\mathcal{J}_{dMe}=6.5$		
Me	4.99	≈ 7.62	—	—	$\mathcal{J}_{cMe}=6.5$		
Me'	5.45	≈ 8.08	—	—	—		

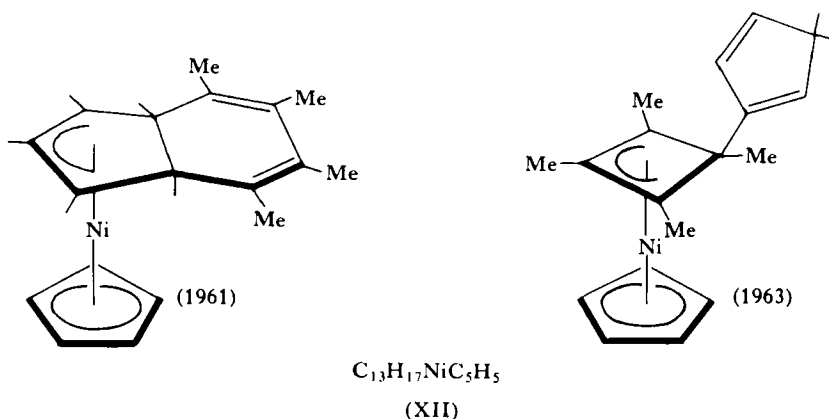
TABLE XIV—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
$\text{C}_7\text{H}_{11}\text{Co}(\text{CO})_2\text{P}(\text{Ph})_3$	5.75	≈ 8.38	—	—	—	$\delta_{\text{C}_6\text{H}_6}(\text{ext}) = 0$	163
	5.33	≈ 7.96	—	—	—		
	4.83	≈ 7.46	—	—	—		
	4.57	≈ 7.20	—	—	—		
	3.00	≈ 5.63	—	—	—		
	1.80	≈ 5.43	—	—	—		
	-0.42	≈ 2.21	—	—	—		
$\text{C}_8\text{H}_{13}\text{Co}(\text{CO})_2\text{P}(\text{Ph})_3$	3.90	≈ 6.53	—	—	—	$\delta_{\text{C}_6\text{H}_6}(\text{ext}) = 0$	163
	4.93	≈ 7.56	—	—	—		
	5.65	≈ 8.28	—	—	—		
	6.91	≈ 9.54	—	—	—		
$[\text{MeOCMe}_2\text{C}_3\text{H}_4\text{PdBr}]_2$							
H ₁	—	4.56	—	—	$\gamma_{12} = 6.4$	CHCl ₃ , 60 Mc/sec	306
H ₂	—	5.96	—	—	$\gamma_{13} = 12.3$		
H ₃	—	7.08	—	—	$\gamma_{14} = 11.4$		
H ₄	—	6.14	—	—	—		
H ₉	—	8.57	—	—	—		
H ₁₀	—	6.70	—	—	—		

^a Tentatively assigned by authors as *syn* isomer, but in view of coupling constants reported, and later assignments by others for similar types of compounds, it is listed here as the *anti* isomer.

^b Resonances were not assigned by original authors; present tentative assignment based on chemical shift patterns of similar types of compounds reported in this review.

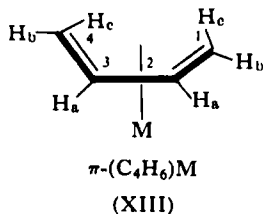
The unusual derivative $C_{13}H_{17}NiC_5H_5$ (XII) obtained from tetramethylcyclobutadiene, nickel dichloride, and sodium cyclopentadienide was believed in 1961 to contain a cyclopentenyl ring system. Subsequently, it was suspected that this might not be the correct structure since the proton NMR showed, among other features, that the four methyl groups are each different from one another (193) (see also Table XIV). Preliminary indications from an X-ray crystallographic study (78) point to an alternative structure, containing a cyclobutenyl ring, which would also account for the observed NMR data.



Olefin Complexes Containing the $\pi-(C_4)M$ System. Cyclobutadiene is the simplest example of an olefin having a $\pi-(C_4)M$ system. Complexes are known in which this ring system is believed to be present, for example, tetramethylcyclobutadiene-nickel dichloride (75a) or of nickel salts (129a). No magnetic resonance data are yet available for these compounds.

The complex first formulated as $C_4H_4Ag^+$, NO_3^- (19a, 20) has been reinvestigated (19). The single resonance at $\tau = 2.9$ in water or D_2O solution may be that of a decomposition or rearrangement product formed shortly after the complex is dissolved. This same resonance is observed when an authentic sample of the complex between *syn*-tricyclooctadiene and silver ion is allowed to age in solution. When freshly prepared, the complex of tricyclooctadiene (see Table X) gives two resonances in D_2O , at $\tau = 2.74$ and 5.83, which are of equal intensity. Therefore, the former assignment of $C_4H_4AgNO_3$ (20) which was based mostly on the single resonance in solution, is now open to question. It is obvious that some changes with time occur for these complexes in solution; further details have been promised (19).

The parent olefin for the majority of $\pi-(C_4)M$ complexes (XIII) is butadiene, for which three resonances with intensity ratios 1:1:1 are observed (see Table XV). When the olefin becomes complexed to a transition



metal, the three groups of resonances assume approximately the same positions as the resonances of the three types of protons in the π -allyl group. The lowest field resonances in the butadiene complexes are assigned as the H_a protons, observed near $\tau = 4$ or 5. These are at only slightly higher field than the resonances of the corresponding protons in the free olefin ($\tau = 3.8$, see Table XV). The other protons appear near $\tau = 9$, a shift of about 4 ppm to higher field in the complex compared to the free olefin.

Before an attempt is made to arrive at a quantitative explanation for the chemical shifts observed for protons in these (or any other) systems, a detailed knowledge of the structure and the placement of the hydrogen atoms is indispensable. In the butadiene complex, $(C_4H_6)Fe(CO)_3$, the placement of the olefin with respect to the iron tricarbonyl group by X-ray diffraction studies (250) does not lead to unequivocal positions for the hydrogen atoms. These could, on the one hand, all be coplanar with the carbon atoms, as implied in the representation (XIII) for $\pi-(C_4H_6)M$. On the other hand, by analogy with recent structural work on cyclopentadiene complexes (see below) there is a good chance that the hybridization for the terminal carbon atoms of the diene system is departing from sp^2 (toward sp^3). If so, the four terminal hydrogen atoms would be displaced from the plane containing the other atoms of the ligand, as might be represented by the structure (XIV) [cf. structure (III) of Mills and Robinson (250)].

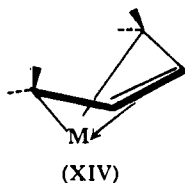


TABLE XV

SUMMARY OF MAGNETIC RESONANCE DATA FOR MISCELLANEOUS OLEFIN COMPLEXES CONTAINING THE π -(C₄)M SYSTEM, AND FOR SOME OF THE FREE OLEFINS

Compound	δ (ppm)	τ [$\delta(\text{CH}_3)_4\text{Si} = 10$]	Relative Intensity	Multi- plicity	J (cps)	Remarks	References
(C ₄ H ₆)Fe ₂ (CO) ₆ (see text for figure)	—	3.52 ^a	—	2 × 3	(see text)	40 Mc/sec, 21° ± 1°	149
C ₄ H ₆ , butadiene $\begin{array}{c} \diagup \text{CH} \\ \diagdown \end{array}$ = CH ₂	—	3.8	(2)	c	—	40 Mc/sec, 21° ± 1°, liquid	148
C ₄ H ₆ · Fe(CO) ₃ (see text for figure)	—	4.89	(4)	3	—		
H _a	—	4.72	(2)	c	6.9	40 Mc/sec, 21° ± 1°	148
H _b }	—	8.32	(2)	2	4.1, 2.5		
H _c }	—	9.78	(2)	2 × 2	4.1, 2.1		
1,2,3,4-Tetraphenylbutadiene-Fe(CO) ₃ ϕ $\begin{array}{c} \diagup \text{CH} \\ \diagdown \end{array}$	—	2.84 3.08	— (20)	— 2	— ~10	40 Mc/sec	148
C ₅ H ₈ OFe(CO) ₃	—	7.62	(2)	—	—		
C ₅ H ₈ OFe(CO) ₃	—	7.54 ^a	—	—	(see text)		149
H _a	—	4.11	(2)	3	—	Not well resolved	149
H _b	—	5.92	(2)	3	—		
[C ₅ H ₈ OFe(CO) ₃] ₂ · hydroquinone							
H _a	—	4.16	(2)	1	—	Reported as	149
H _b	—	5.88	(2)	1	—	(C ₁₁ H ₇ O ₃)Fe	
Hydroquinone	—	3.36	(2)	1	—		
C ₅ H ₈ Fe(CO) ₃ (isoprene) $\begin{array}{c} \diagup \text{CH} \\ \diagdown \end{array}$ CH ₃	—	5.02	(1)	—	—		200
	—	7.85	(3)	—	—		
	—	8.3	(2)	—	—		
	—	8.5	(2)	—	—		
	—	9.58	(2)	—	—		
	—	9.72	(2)	—	—		
	—	9.95	(2)	—	—		
==CH ₂							

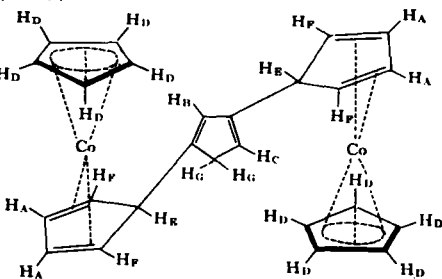
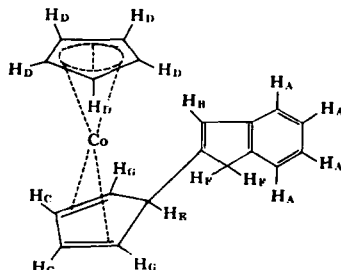
TABLE XV—continued

Compound	δ (ppm)	τ [$\delta(\text{CH}_3)_4\text{Si} = 10$]	Relative Intensity	Multiplicity	γ (cps)	Remarks	References
C_6H_{10} , 2,3-dimethyl-1,3-diene =CH ₂	—	5.2	—	—	—		379
$(\text{C}_6\text{H}_{10})_2\text{Co}_2(\text{CO})_4$ =CH ₂	—	{ 7.84 8.37 8.19	— — —	— — —	— — —	56.5 Mc/sec	379
C_5H_8 , cyclopentadiene CH ₃ =CH CH ₂	— — —	 3.62 7.21	 (4) (2)	 c 5	 <1 ~1.2	40 Mc/sec	148 348 360
$\text{C}_5\text{H}_6 \cdot \text{Ag}^+$, ClO_4^- =CH CH ₂	— — —	 2.93 6.68 (5.73) ^b (2.60) ^b	— — — —	— — — —	— — — —	Acetone soln	360
$\text{C}_5\text{H}_8\text{RhC}_5\text{H}_5$ C ₅ H ₅ H _a H _b CH ₂	— — — — —	 4.87 ~4.91 6.75 { 6.66 7.08	 (7) (2) (1) (1)	 2 3 or 4 2 2	 — 1-2 — 11.2 11.2	40 Mc/sec Also taken at 60 Mc/sec	148
$\text{C}_5\text{H}_8\text{CoC}_5\text{H}_5$ C ₅ H ₅ H _a CH ₂ H _b	— — — — —	 5.41 4.80 { 7.32 7.99 7.57	 (5) (2) (1) (1) (2)	 1 3 2 2 5	 — ~2 12.7 12.7 —	40 Mc/sec Also taken at 60 Mc/sec	148
$(\text{C}_5\text{H}_5\text{D})\text{CoC}_5\text{H}_5$ C ₅ H ₅ H _a H _b CDH	— — — — —	 5.42 4.80 7.60 7.36	 (5) (2) (2) (1)	 1 3 4 5	 — 2 ~2 2.1	40 Mc/sec	148
$\text{C}_5\text{H}_6\text{FeC}_6\text{H}_6$ $(\text{C}_5\text{H}_5\text{D})\text{FeC}_6\text{H}_6$							

See $\text{C}_6\text{H}_7\text{FeC}_5\text{H}_5$, Table XVIII
See $\text{C}_6\text{H}_6\text{DFeC}_5\text{H}_5$, Table XVIII

$(\text{CH}_6)\text{Fe}(\text{CO})_2\text{P}\phi_3$						
C_6H_5	—	2.73	(15)	2	$\text{P}^{31}\text{-H}$, 5.2	56.43 Mc/sec
H_a	—	4.87	(2)	2×2	Overlapping	84
H_b	—	7.5	(4)	—	—	
CH_2	—	7.19	—	—	AB pattern	
		7.38	—	—		
		8.0	—	—		
<i>Substituted Cyclopentadienes</i>						
$(\text{C}_5\text{H}_5\text{CH}_3)\text{CoC}_5\text{H}_5$						
C_5H_5	—	5.39	(5)	1	—	40 Mc/sec
H_a	—	4.93	(2)	3	2	148
H_b	—	7.37	(3)	c	—	
$\text{CH}(\text{CH}_3)$	—	9.77	(3)	2	5.8	
CH_3	—					
$(\text{C}_5\text{H}_5\text{CHCl}_2)\text{CoC}_5\text{H}_5$						
C_5H_5	—	5.25	(5)	1	—	40 Mc/sec
H_a	—	4.88	(2)	3	2	148
CHCl_2	—	6.00	(1)	2	8.9	
$\text{CH}(\text{CHCl}_2)$	—	7.86	(3)	c	—	
H_b	—	8.11				
$(\text{C}_5\text{H}_5\text{CCl}_3)\text{CoC}_5\text{H}_5$						
C_5H_5	—	5.25	(5)	1	—	40 Mc/sec
H_a	—	4.77	(2)	3	2	148
$\text{CH}(\text{CCl}_3)$	—	6.30	(1)	3	2.5	365
H_b	—	7.40	(2)	2×2	4.2, 2.2	173
$(\text{C}_5\text{H}_5\text{CF}_3)\text{CoC}_5\text{H}_5$						
$\text{CH}(\text{CF}_3)$	—	—	—	3×4	—	
$(\text{C}_5\text{F}_4)(\text{C}_5\text{H}_5\text{CoC}_5\text{H}_5)_2$						
H_a	—	5.08 ^c	—	3	2	$\delta_{\text{F}^{19}}$ for CF_3 , doublet,
$\text{CH}(\text{CF}_2^-)$	—	3.1 ^c	—	(very weak)	—	from $\mathcal{J}_{\text{CH}-\text{CF}_3}$ 173
C_5H_5	—	4.62 ^c	—	1	—	F^{12} ($\delta\phi_{\text{CF}^3}=0$) 173
H_b	—	2.37 ^c	—	—	—	62.2 ppm, doublet
						$\mathcal{J}_{\text{CH}-\text{CF}_2}=13.5$ cps

TABLE XV—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	J (cps)	Remarks	References
(C₅H₄)(·C₅H₅CoC₅H₅)₂							
	H _A	—	4.8	(4)	3	CS ₂ soln, 60 Mc/sec	131
	H _B	—	4.8	(1)	Obscured		
	H _C	—	4.92	(1)	3		
	H _D	—	5.27	(10)	1		
	H _E	—	6.50	(2)	c		
	H _F	—	7.28	(4)	3+c		
	H _G	—	7.81	(2)	4		
(C₅H₅·C₉H₇)CoC₅H₅							
	H _A	—	2.98	(4)	c	CS ₂ soln, 60 Mc/sec Also reported for benzene soln	131
	H _B	—	4.5	(1)	4		
	H _C	—	4.87	(2)	3		
					A_2B_2 $J_{AB} = 8.4$ $J_{AB} = 1.6$		
					$A_2X_2(x = H_F)$ $J_{AA'} + J_{AX'} = 4$		
	H _D	—	5.3	(5)	1		
	H _E	—	6.5	(1)	4		
	H _F +H _G	—	7.1	(4)	c		

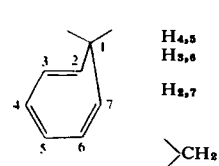
Cyclohexadienes

C₆H₈, cyclohexa-1,3-diene

	—	4.22	(4)	2	~ 2	22' ± 1°	48
	—	7.92	(4)	—	~ 4	CCl ₄ soln	
C ₆ H ₈ Fe(CO) ₃	—	4.77	(2)	Λ ₂ X ₂	$\gamma_{aa} = 4.1$		48
H _a	—	6.86	(2)	2 × 3	$\gamma_{ab} = 6.6$		
	—	8.37	(4)	—	$\gamma_{ab'} = 1.5$		
(C ₆ H ₈) ₂ Mo(CO) ₂ ^d	—	5.8	(1)	1	—	60 Mc/sec	132
H _a	—	7.4	(1)	1	—		
H _b	—	8.5	(2)	2	5.7		
(C ₆ H ₈)Co(C ₅ H ₈)	—	5.21	(2)	—	—		204
H _a	—	5.37	(5)	—	—		
C ₅ H ₈	—	7.00	(2)	—	—		
H _b	—	8.76	(2)	—	—		
	—	9.29	(2)	—	—		
C ₆ H ₈ FeC ₆ H ₈	—	5.13	(6)	1	—		121
C ₆ H ₈	—	5.42	(2)	2 × 2	—		
H _a	—	7.48	(2)	—	—		
H _b	—	~ 8.6	(4)	—	—		
	—	~ 8.6	(4)	—	—		
C ₆ H ₈ OsC ₆ H ₈	—	5.08	6	—	—		120
C ₆ H ₈	—	4.68	2	—	—		
C ₆ H ₈	—	8.58	2	—	—		
C ₆ H ₈	—	8.08	4	—	—		
C ₆ H ₈ RuC ₆ H ₈	—	5.0	(6)	1	—	56.45 Mc/sec	181
C ₆ H ₈	—	5.48	—	—	$\gamma_{aa} = 3.4$	CCl ₄ soln	
H _a	—	5.6	(2)	Λ ₂ X ₂	$\gamma_{ab} = 5.6$	This compound may	
H _b	—	7.16	—	—	$\gamma_{ab'} = 1.1$	also exist in isomeric	
	—	8.73	(4)	3	—	form, as (C ₆ H ₇) ₂ Ru,	
C ₆ F ₈ , perfluorocyclohexa-1,3-diene	—	63.20	—	3 + c	13.2	Liquid	
	—	91.55	—	3	15.2	$\delta_{F^{19}}(\phi CF_2) = 0$	173
F _a	—	100.9	—	5 × 4	30.6		
F _b	—	100.9	—	(?)	13.4		
					1.5		

TABLE XV—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	J (cps)	Remarks	References
$\text{C}_6\text{F}_5\text{Fe}(\text{CO})_3$							
>CF_2	35.4	—	—	—	$J_{\text{CF}_1-\text{CF}} = 18.2$	CCl_4 soln $\delta_{\text{F}^{19}}(\phi\text{CF}_3) = 0$	173
F_a	54.70	—	—	—	$J_{\text{AB}} = 232$		
F_b	119.4	—	—	3×3	$J_{\text{CF}_2-\text{CF}} = 14.2$		
	139.5	—	—	5×4 (?)	$\begin{cases} 19.4 \\ 3.4 \\ 18.2 \\ \sim 3 \end{cases}$		
$(\text{CH}_3)_3\text{C}_6\text{H}_5\text{Fe}(\text{CO})_3$							
<i>Substituted Cyclohexadienes</i>							
	—	4.83	—	—	—	200	
$\text{>CH}(\text{CH}_3)$	—	7.08	—	—	—		
>CH_2	—	7.85	—	—	—		
$(\text{CH}_3)_a$	—	7.93	—	—	—		
$(\text{CH}_3)_b$	—	8.45	—	—	—		
$\text{>CH}(\text{CH}_3)$	—	9.07	—	2	$J_{\text{CH}-\text{CH}_2}$		
$(\text{C}_8\text{H}_6 \cdot \text{C}_2\text{H}_4)\text{CoC}_5\text{H}_5$ C_8H_{10} , bicyclo[4,2,0]octa-2,4-diene (see text for figure)							
H_a	—	4.96	(2)	—	—	Fine structure not determined.	204
C_5H_5	—	5.38	(5)	—	—		
H_b	—	6.87	(2)	—	—	60 Mc/sec, CS_2	
$\text{>CH}-\text{CH}_2$	—	7.79	(2)	—	—		
$\text{>CH}-\text{CH}_2$	—	8.44	(2)	—	—		
$\text{>CH}-\text{CH}_2$	—	9.14	(2)	—	—		
$(\text{C}_8\text{H}_6 \cdot \text{C}_2\text{H}_4)\text{Fe}(\text{CO})_3$							
H_a	—	4.64	(2)	A_2X_2	$(x = \text{H}_b)$	CCl_4 soln	48
H_b	—	6.63	(2)	—	$J_{\text{AA}} = 4.8$		
>CH	—	7.45	(2)	—	$J_{\text{AX}} = 6.8$		
>CH_2	—	8.16	(4)	A_2B_2	$J_{\text{AX}'} = 1.6$		
	—	8.83	—	—	—		



Cycloheptatriene

H_{4,5}
H_{5,6}H_{2,7}>CH₂C₇H₈ · Fe(CO)₃
(iron bonded to C_(4,5,6, and 7))H₃
H₂H_{3,6}
H₄
H₇>CH₂(C₇H₈ · H⁺)Fe(CO)₃ }
(C₇H₈ · D⁺)Fe(CO)₃ }C₇H₈FeC₇H₁₀A
B
C
D
F

Cycloheptadiene

C₇H₁₀

>CH

(>CH₂)₂>CH₂C₇H₁₀ · Fe(CO)₃H_a
H_b(>CH₂)₂>CH₂C₈H₈

Cyclooctatetraene

—	3.49	—	c	—
—	3.91'	—	2 × 3	$\mathcal{J}_{(4,5), (2,6)} = 3.1$
—	4.73	—	AB pairs	$\mathcal{J}_{AB} = 9$
—		—	2 × 3	$\mathcal{J}_{(2,7), (1,1)} = 6.7$
—	7.81	(2)	3	$\mathcal{J}_{(2,7), (1,1)} = 6.7$
—	4.85	—	c	—
—	4.87	—	AB pair	—
—	4.76	—	c	—
—	6.70	—	A ₂ X ₂	$\mathcal{J}_{AA} = 4.74$
—	7.04	—	c	(H _x = H ₄ or H ₇)
—	7.62	—	c	$\mathcal{J}_{AX} = 7.7$
—	7.73	—	c	$\mathcal{J}_{AX'} = 1.5$

See π -(C₃)M derivatives, Table XVIII

—	5.18	2	—	—
—	5.98	4	—	—
—	6.29	4	—	—
—	7.71	4	—	—
—	8.80	4	—	—

A, B and C are the 120a
 π -bound part of the ligand

—	4.31	—	c	—
—	7.69	—	c	—
—	8.08	—	c	—
—	4.76	(2)	—	$\mathcal{J}_{AA} = 4.75$
—	6.99	(2)	A ₂ X ₂	$\mathcal{J}_{AX} = 7.6$
—		—	—	$\mathcal{J}_{AX'} = 1.2$
—	8.05	(4)	c	—
—	8.55	(2)	c	—

171 cps ~ 4.3

Low-field side of 228
cyclohexane; 40 Mc/sec

48

48
80

48

48
80

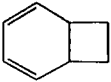
$C_8H_{10}Fe_2(CO)_8$	—	5.47	2	2×2	—	CS_2 soln	196
	—	6.08	2	$2 \times 2 \times 2$	—		
	—	7.35	2	6	—		
	—	7.96	2	6	—		
	—	8.47	2	5	—		
$C_8H_{10}Fe(CO)_3$ Free olefin	—	4–5	4	—	—	Complex, well-resolved band	247
H_a	—	6.51	1	3	—	Unsymmetrical	
H_b	—	6.86	1	3	—	Unsymmetrical	
CH_3	—	7.9, 8.5	4	—	—		
$C_8H_{10}Mo(CO)_3$	—	4.15	2	2×2	—		196
	—	4.86	2	$2 \times 2 \times 2$	—		
	—	5.31	2	5	—		
	—	7.9	2	C	—		
	—	8.7	2	—	—		
$C_8H_{10}CoCp$							
 $CoCp$							
Free olefinic H's	—	4.62	1	—	—		247
Bonded olefinic H's	—	6.46	2	—	—		
CH_3	—	7.2, 8.5	—	—	—		
Inner	—	4.92	2	4	—		
Outer	—	6.86	2	—	—		247
Bridgehead	—	7.69	2	—	—		
CH_3	—	8.92	4	—	—		
<i>Other Miscellaneous Ligands</i>							
$C_7H_{10}OFe(CO)_3$	—	4.39	1	—	—		196
$Me_2C:CHC(Me):CO$ or	—	8.10	3	—	—		
$Me_2C:C(Me)CH:CO$	—	8.22	3	—	—		
	—	8.20	3	—	—		

TABLE XV—continued

Compound	δ (ppm)	τ [$\delta(\text{CH}_3\text{Si}) = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
$[\text{C}_6\text{H}_5\text{Fe}(\text{CO})_3]_2$	—	4.81	2	—	—	CCl_4 Two diastereomers unidentified	223
	—	8.24	1	—	—		
	—	8.89	5	—	—		
	—	9.74	1	—	—		
	—	4.83	2	—	—		
	—	8.28	1	—	—		
	—	8.92	5	—	—		
	—	9.77	1	—	—		
Tropone iron tricarbonyl	—	3.4	2	C	—		196
	—	5.09	1	$2 \times 2 \times 2$	—		
	—	6.91	1	5	—		
	—	7.29	2	3	—		
$\text{C}_6\text{H}_5\text{OFe}(\text{CO})_3$	—	3.8	2	C	—		196
	—	4.43	2	3	—		
	—	6.59	1	3	—		
	—	7.10	2	2	—		
	—	7.72	1	3	—		

^a Center of symmetry, double triplet pattern, A_2B_2

^b Decomposition product.

^c The authors claim their proton resonances are listed as τ -values; however, from the discussion in their text, it is clear that H_b should be at higher field than H_a , so it is suspected that these [and possibly all the resonances reported, especially the low value for $-\text{CH}(\text{CF}_3)$] are unconverted δ values (chemical shifts on the low side of Me_4Si).

^d This compound may also exist in isomeric form as $\text{C}_6\text{H}_5\text{Mo}(\text{CO})_3(\text{C}_6\text{H}_7)$, see Table XIV or XVIII.

^e Center calculated for each of an AB pair.

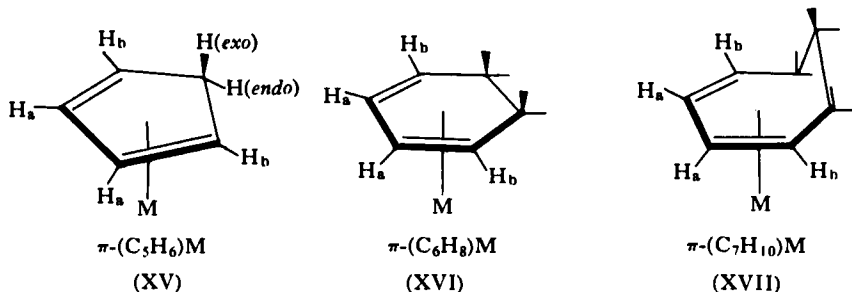
^f Center calculated for each of an AB pair.

^g Center calculated for each of an AB pair.

The NMR spectra of butadiene complexes (XIII) are interpretable in terms of an $A_2B_2X_2$ system. The resonance for the H_a protons would be expected to be a triplet of triplets. The larger spacing would correspond to the coupling constant between H_a and the two H_c protons. Because each H_a proton is strongly coupled to the other, there would be some contribution to the coupling of an H_a proton with the distant H_c proton [see Pople, Schneider, and Bernstein (290) or the discussion of "virtual coupling" by Musher and Corey (261)]. The long-range interaction would be expected to be small (though detectable) and this would lower the net observed coupling constant $\mathcal{J}_{H_a-H_c}$. The larger triplet separation should be an average of the coupling constants $\mathcal{J}_{H_a-H_b}$ (vicinal) and $\mathcal{J}_{H_a-H_c}$ (long-range). If the latter is close to zero, then the effective coupling constant should be about half the "normal" vicinal coupling constant, which would depend, in turn, upon the dihedral angle between the protons in this rigid system (186). Similar arguments hold for the smaller triplet separation in the resonance of proton H_a . This proton is also in a vicinal position relative to proton H_b , and there should be two coupling constants $\mathcal{J}_{H_a-H_b}$ (vicinal) and $\mathcal{J}_{H_a-H_b'}$ (long-range); the observed coupling should be an average of these, and again, if the long-range coupling is close to zero, the observed smaller triplet separation should be about half the "normal" coupling.

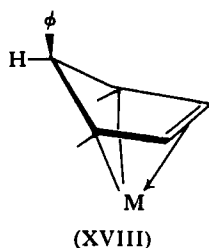
The fine structure in the resonance for H_b would be expected to be a triplet with splitting equal to the smaller triplet separation for H_a ; for H_c , a triplet of separation equal to the larger separation of triplets in H_a would be expected. The coupling between H_b and H_c is a geminal interaction and could be very small; it is, in fact, not normally resolved under present instrumental conditions. With more rigorous analysis, it is also possible to derive the coupling constant $\mathcal{J}_{H_b-H_c}$ in this system; this is reported for some of the derivatives containing the $\pi-(C_4)M$ system (see Table XV). It has been observed generally to be in the range of 4 to 5 cps.

The diene bonding system may also be part of a larger carbocyclic ring bonded to a metal, as for instance in complexes of pentadiene, $\pi-(C_5H_6)M$ (XV); hexadiene, $\pi-(C_6H_8)M$ (XVI), or heptadiene, $\pi-(C_7H_{10})M$ (XVII) (see Table XV). In these, the protons H_c of butadiene are replaced by one or more methylene groups which introduce further complexities in the NMR spectra. In the pentadiene derivatives, of which $(C_5H_6)Fe(CO)_2P\phi_3$ (84) may serve as an example, the resonance of the H_a protons is found at $\tau = 4.9$, and that of the H_b protons at $\tau = 8.0$. These chemical shifts follow reasonably closely those assigned for the corresponding protons in the butadiene com-



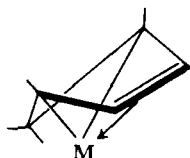
plex, $(\text{C}_4\text{H}_6)\text{Fe}(\text{CO})_3$, even though there are other differences in the complexes being compared. The ring protons H_a and H_b have been analyzed as an A_2B_2 system and the coupling constants arrived at for $\mathcal{J}_{\text{A-A}}$, $\mathcal{J}_{\text{A-B (cis)}}$, and $\mathcal{J}_{\text{A-B (distant)}}$ are of comparable magnitude to analogous coupling constants in related complexes. The H_b protons show further coupling to the methylene protons (see Table XV).

Owing to the geometry of these carbocyclic ring complexes, the two methylene protons are shielded to different extents. In the IR spectrum, one of these is seen to absorb at an anomalously low frequency for a C—H stretching mode, $2700\text{--}2800\text{ cm}^{-1}$, and it was shown that this same proton was associated with the more shielded of the two resonances attributed to the methylene protons. (148). These spectroscopic properties were tentatively assigned to the *endo* proton (nearer the metal atom). More recently, however, a single-crystal X-ray diffraction analysis of the related cyclopentadiene derivative containing a phenyl group substituted on the methylene carbon atom, $(\text{C}_5\text{H}_5\phi)\text{CoC}_5\text{H}_5$, indicated a structure (XVIII) in which the phenyl group occupied the *exo* position with respect to the metal atom (62). This



derivative did not have an anomalously low C—H stretching frequency assigned to an *endo* proton on the methylene group, although it undoubtedly contained one. It is likely, therefore, that the present assignments of

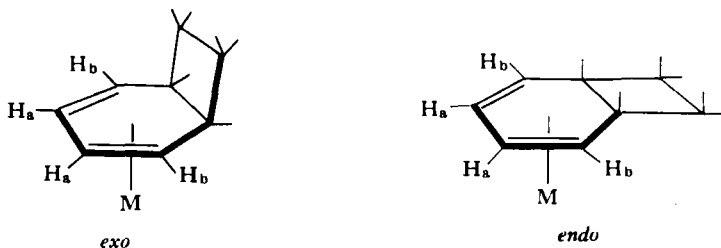
stretching frequencies and chemical shifts of the methylene protons are reversed. It was proposed (62) that the assignment in other cyclopentadiene derivatives might be correct as originally given if the methylene group in these complexes were bent *toward* the metal, as in (XIX). However, from molecular models it can be seen that the disposition of the carbon orbitals



(XIX)

in (XIX) would be quite unfavorable for overlap with the metal orbitals and this structure can be considered as extremely unlikely. Nevertheless sufficient ambiguity remains at this time that assignment of methylene protons in these carbocyclic systems has been omitted in Table XV.

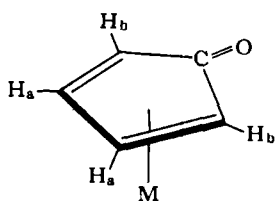
Complexes of cyclohexadiene (XVI) or cycloheptadiene (XVII) have also been studied; the data for these are included in Table XV. The protons of the diene system form an A_2B_2 pattern, with additional splitting (mainly of the resonance H_b) arising from the methylene protons. Again, complete assignments for the methylene protons could not be made for these systems, since structural information is lacking. The same would apply to substituted cyclohexadiene complexes, such as bicyclo[4.2.0]octa-2,4-diene (XX) (see Table XV). It is not known whether the four-membered ring is fused *endo* or *exo* with respect to the position of the metal atom. Assignment of methylene and of methine proton resonances must therefore remain partly ambiguous.



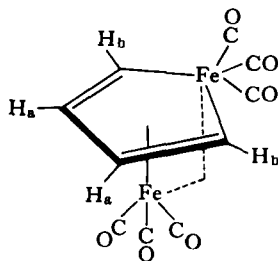
$\pi-(C_8H_{10})M$
(XX)

Complexes such as 2,3-dimethylbutadiene-dicobalt hexacarbonyl contain a $\pi-(C_4)M$ system in which the H_a protons of the original butadiene system have been replaced by alkyl group(s). These, and other examples of substituted $\pi-(C_4)M$ derivatives are also listed in Table XV. The complexes of 5,6-dimethylenebicyclo[2.2.1]heptene-2 (already mentioned under chelating olefins, see Table XI) should also be considered here, as they contain the $\pi-(C_4)M$ system in which a ring system has been fused into the positions occupied by H_a protons in the parent butadiene complex.

The $\pi-(C_4)M$ system has also been observed in ring systems in which a rather simpler situation from the spectroscopic viewpoint exists than in the parent olefin. Two such examples are the complexes of cyclopentadienone (XXI) or the unusual binuclear complex obtained from an iron carbonyl and acetylene, $C_4H_4 \cdot Fe_2(CO)_6$ (XXII) (Table XV). The proton resonances in these complexes may be analyzed simply as A_2B_2 systems. Details on the structures, especially the position of the protons in these complexes, is not yet known.



$\pi-(C_5H_4O)M$
(XXI)



$(C_4H_4) \cdot Fe_2(CO)_6$
(XXII)

The complex of cyclooctatetraene-iron tricarbonyl shows only a single line in the proton spectrum (see Table XV). In this complex, a C_4 system of the ligand interacts with the metal atom (91a), rather than two separate olefinic bonds, as in some of the chelating $\pi-(C_2)_2M$ systems in complexes of cyclooctatetraene mentioned above. The single line spectrum observed for the protons is now believed to represent an averaged chemical shift arising from valence tautomerism of the $Fe(CO)_3$ group around the olefinic ring (see section III, B, below).

The complex $C_8H_8Fe(CO)_3$ resists hydrogenation by the usual catalytic means. It may, however, be attacked by a proton, which converts it into a cationic derivative [discussed under $\pi-(C_5)M$, below] and subsequently

Nuclear Magnetic Resonance

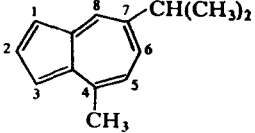
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TABLE XVI—continued

Compound	τ [$\delta(\text{CH}_4)_{\text{SI}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
$\text{C}_{10}\text{H}_6\text{D}_2\text{Fe}_2(\text{CO})_5$						
H _{5,7}	~4.66	(~2)	c	—		47 ^a
H _{2,4}	~4.9	(~2)	—	—		
H ₈	4.77	(1)	2 × 2	$\begin{cases} \gamma_{8,7} = 5.8 \\ \gamma_{8,6} = 1.4 \end{cases}$		
H ₆	6.54	(1)	3		$\gamma_{6,5}\gamma_{6,7} \simeq 8.5$	
$\text{C}_{11}\text{H}_{10}$, 4-methylazulene						
H ₈	1.90	(1)	2	$\gamma_{8,7} = 9.0$		47 ^a
H ₂	2.30	(1)	3	$\gamma_{2,1}\gamma_{2,3} = 3.9$		
H _{1,3}	2.77	(2)	2 × 2	—		
CH ₃	7.31	(3)	1	—		
H _{5,6,7}	2.90	—	2	1.7		
	3.04	—	—	—		
	3.08	—	—	—		
	3.18	—	—	—		
	3.25	—	2	1.5		
	3.36	—	—	—		

C ₁₁ H ₁₀ Fe ₂ (CO) ₅ (mixture of isomers whose protons are designated H and H')		4.55	(10)	—	—	For CH ₃ in position 4 these peaks assigned to H _{2, 3, 5, 7, 8} . For CH ₃ in position 8 assigned to H _{2, 3, 4, 5, 7}	47 ^a	
		4.70						
		4.73						
		4.88						
		4.92						
		5.03						
		5.15						
		5.24						
		5.37						
H ₁		6.13	(1)	"3"	$\gamma_{1,3}\gamma_{1,2} = 2.2$	Neither H ₁ and H _{1'} or H ₆ and H _{6'} have been assigned to specific isomer		
H _{1'}		6.34	(1)	2 × 2	$\begin{cases} \gamma_{1,2} = 2.8 \\ \gamma_{1,3} = 1.8 \end{cases}$			
H ₆		6.62	(1)	"3" × 2	$\begin{cases} \gamma_{5,6}\gamma_{6,7} \simeq 7.9 \\ \gamma_6 = 1.4 \end{cases}$			
H _{6'}		6.76	(1)	"3" × 2	$\begin{cases} \gamma_{6,5}\gamma_{6,7} \simeq 7.2 \\ \gamma_6 = 1.7 \end{cases}$			
CH ₃		8.42	(3)	2 × 2 × 2	$\gamma_{4,5} = 1.3$			
C ₁₃ H ₁₄ , 4,6,8-trimethylazulene								
H ₂		2.50	(1)	3	$\gamma_{2,3} = 3.9$	47 ^a		
H _{1,3}		2.85	(2)	2 × 2	$\gamma_{1,2} = 3.9$			
H _{5,7}		3.25	(2)	1	—			
(CH ₃) _{4,8}		7.32	(6)	1	—			
(CH ₃) ₆		7.6	(3)	1	—			
C ₁₃ H ₁₄ Fe(CO) ₃						47 ^a		
H _{2, 3, 5, 7}		4.77	(4)	c	—			
		4.80						
		4.82						
		4.76						
		4.93						
		4.97						

TABLE XVI—*continued*

Compound	τ [$\delta(\text{CH}_3)_4\text{Si} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
H ₁	6.15	(1)	2 × 2	$\begin{cases} \mathcal{J}_{1,2} = 2.9 \\ \mathcal{J}_{1,3} = 1.9 \end{cases}$		
(CH ₃) ₈	3.90	(3)	1	—		
(CH ₃) ₆	8.24	(3)	1	—		
(CH ₃) ₄	8.39	(3)	2	$\mathcal{J}_{\text{CH}_3-\text{H}(4)} = 1.4$		
C ₁₅ H ₁₈ , guaiazulene						
						
H ₈	1.93	(1)	2	$\mathcal{J}_{8,6} = 1.9$		47 ^a
H ₂	2.50	(1)	2	$\mathcal{J}_{2,3} = 3.9$		
H ₆	2.80	(1)	2 × 2	$\begin{cases} \mathcal{J}_{6,5} = 11.2 \\ \mathcal{J}_{6,8} = 1.8 \end{cases}$		
H ₃	2.94	(1)	2	$\mathcal{J}_{2,3} = 3.9$		
H ₅	3.21	(1)	2	$\mathcal{J}_{5,6} = 11.2$		
CH(CH ₃) ₂	7.03	(1)	5 of 7	$\mathcal{J}_{\text{CH}(\text{CH}_3)_2} = 6.8$		
CH ₃ (4)	7.29	(3)	1	—		
CH ₃ (1)	7.37	(3)	1	—		
CH(CH ₃) ₂	8.69	(6)	2	6.8		

$C_{15}H_{18}Fe_2(CO)_5$ Isomer B (see text)
 $(CH(CH_3)_2)$ in position 7, CH_3 groups in
 1 and 4)

H_5	4.70	(1)	2×4	$\begin{cases} \mathcal{J}_{5,6} = 8.9 \\ \mathcal{J}_{5-CH_3(4)} \sim 1.4 \end{cases}$	56.4 and 40 Mc/sec	47 ^a
H_2	4.90	(1)	2	$\mathcal{J}_{2,3} = 2.9$		
H_3	5.04	(1)	2	—		
H_8	5.33	(1)	2	$\mathcal{J}_{8,6} = 1.8$		
H_6	6.76	(1)	2×2	$\begin{cases} \mathcal{J}_{6,5} = 8.9 \\ \mathcal{J}_{6,8} = 2.0 \end{cases}$		
$CH(CH_3)_2$	7.37	(1)	5 of 7	$\mathcal{J}_{CH(CH_3)_2} = 6.7$		
$CH_3(1)$	8.47	(3)	1	—		
$CH_3(4)$	8.51	(3)	2	$\mathcal{J}_{CH_3-H(4)} = 1.3$		
$CH(CH_3)_2$	8.59	(6)	2	—		

$C_{15}H_{18}Fe_2(CO)_5$ Isomer A (see text)
 $(CH(CH_3)_2)$ in position 5, CH_3 groups in
 3 and 8)

H ₇	4.79	(1)	2	$\mathcal{J}_{7,6} \simeq 8.5$	47 ^a
H ₄	4.81	(1)	2?	or ~ 1.2	
H ₂	4.98	(1)	2	$\left\{ \mathcal{J}_{2,1} = 2.8 \right.$	
H ₁	6.26	(1)	2		
H ₆	6.92	—	—	$\left\{ \begin{array}{l} \mathcal{J}_{6,4} = 1.6 \\ \mathcal{J}_{6,7} = 8.5 \end{array} \right.$	
CH(CH ₃) ₂	7.83	(1)	5 of 7	$\mathcal{J}_{CH(CH_3)_2} \sim 6.5$	
CH _{3(3,8)}	7.90	(6)	1	—	
CH(CH ₃) ₂	9.06 } 9.09 }	(6)	$\left\{ \begin{array}{l} 2 \\ 2 \end{array} \right.$	— —	

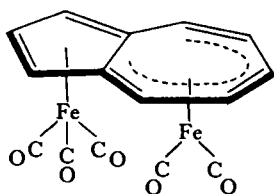
TABLE XVI—continued

Compound	τ [$\delta(\text{CH}_3)_{\text{Si}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
$\text{C}_{10}\text{H}_9\text{CrCp}$						
Cp	6.29	5	—	—		117
H _{3, 3'}	6.05	2	—	—		133
H _{5, 6, 7}	4.36	3	—	—		
H _{4, 8}	3.83	2	—	—		
H _{2, 3}	{ 3.43 2.86	{ 1 1	{ — —	{ — —		
$\text{C}_{13}\text{H}_{15}\text{CrCp}$						
Me _{4, 6, 8}	{ 7.0 7.26 7.11	{ 9	{ — — —	{ — — —		117
Cp	6.37	5	—	—		
H _{1, 1'}	6.2	2	—	—		
H _{5, 7}	4.37	—	—	—		
H _{2, 3}	{ 3.4 2.65	{ 1 ≈ 1	{ — —	{ — —		
$\text{C}_{10}\text{H}_{11}\text{CrCp}$						
H _{2, 2'}	7.55	2	—	—		117
H _{1, 1', 3, 3'}	6.58	4	—	—		
Cp	6.16	5	—	—		
H _{4, 5, 6, 7, 8}	4.37	5	—	—		

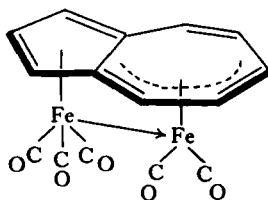
^a Taken from Burton, Pratt, and Wilkinson (47). The spectra were recorded at $22^\circ \pm 1^\circ$ at 56.4 and 40 Mc/sec. The parent azulenes were measured in CCl_4 , and the complexes, in CHCl_3 , CDCl_3 , or CH_2Cl_2 .

neutralized by hydride ion to yield $C_8H_{10}Fe(CO)_3$ (86). In this derivative, the olefin is believed to be bonded to the metal atom through a diene system, and no olefinic bonds remain in the ligand. There is evidence that at some stage of this "ionic hydrogenation" (protonation and subsequent hydride attack) that an olefin containing a bicyclic[5.1.0] system has formed (see Table XV). The principal NMR spectral evidence for the three-membered ring is the very highly shielded proton resonance ($\tau = 10.61$) which is characteristic of such systems, and the H-H coupling constants, see (379a).

Azulene and various substituted azulenes will form complexes with metal carbonyls, such as (azulene) $\cdot Fe_2(CO)_5$ (48). The data for a number of these are summarized in Table XVI. It seems likely that at least one of the two metal carbonyl groupings [the $Fe(CO)_3$ group] is bonded to the olefin through a $\pi-(C_4)M$ system. For the other, the nature of the bond is still ambiguous. It is conceivable that a $\pi-(C_6)M$ system is attached to the $Fe(CO)_2$ (XXIII) [this would fit the Effective Atomic Number (EAN) rule]. However, in view of the tendency of iron to bond to C_4 systems in olefin complexes, and the lack of any well-characterized $\pi-(C_6)-Fe(CO)_2$ complexes of iron, an alternative formulation might be preferable, one in which the $Fe(CO)_2$ group is attached to a C_4 system (XXIV) within the seven-membered ring of azulene, and fulfills its EAN requirement by internal dative bonding from the other iron carbonyl group. There is precedent for this formulation in the complex $C_4H_4 \cdot Fe_2(CO)_6$. Of course still other structures are possible, such as one in which the $Fe(CO)_2$ group is



(XXIII)



(XXIV)

associated with the five-membered ring. The exact structure for these is not yet fully established. In theory, optical isomers of these azulene complexes should exist, but no resolution has yet been achieved. For the case of substituted azulenes, both geometrical and optical isomers are possible, and separation into two isomers has been achieved for the methyl-substituted azulenes. These may be differentiated by their proton spectra (see Table XVI).

Olefin Complexes Containing the π -(C₅)M System. The simplest example of this type of bonding system is the cyclopentadienyl ring (C₅H₅) for which a single sharp resonance is usually observed near $\tau = 5$. A large number of transition metal derivatives are known which contain this π -bonded ring system.⁶ The resonance data reported for these are summarized in Table XVII. The protons of such a ring appear, in general, to be magnetically equivalent; even when other groups around the metal tend to introduce asymmetry, rapid rotation about the metal to ring axis is probably responsible for smoothing out possible anisotropies in the shielding of the ring protons.

The ring proton resonance can be split into multiplets by spin-spin coupling either with isotopes of the metal bonded to it (if $I \neq 0$) or with protons bonded to the metal. The splittings in the former case range from less than 1 cps, as in C₅H₅RhC₅H₆ (86), up to 18.5 cps, as in C₅H₅Pt(CO)I (132a). The splitting of ring protons by protons bonded to the metal have thus far been observed to be small, all on the order of 1 or 2 cps [cf. (C₅H₅)₂ReH or (C₅H₅)₂MoH₂].

A number of transition metal complexes contain the (C₅H₅) group σ -bonded to a metal atom whose NMR should consist of groups of resonances in the relative intensity ratios 1:2:2. This has been observed in a few cases, but often chemical exchange will give an averaged observed chemical shift for σ -bonded cyclopentadienyl ring protons, as in (σ -C₅H₅)Fe(CO)₂ (π -C₅H₅) or dicyclopentadienylmercury (see section III, B, below). Such an averaged resonance line usually appears at a little lower field than is normally expected for the single line of the π -C₅H₅ group.

The electron spin densities at the ring protons have been obtained from a measurement of the contact interaction shift for a number of paramagnetic metallocenes (242, 243) (Table XVII). This has also been discussed by Levy and Orgel (218).

Substituents on the five-membered ring may complicate the proton resonance signal. It will not be possible to give a comprehensive coverage of this type of complex because the organic chemistry of ferrocene in which such substitutions are the main interest has by now grown to large proportions. Magnetic resonance data are given for a limited number of these in Table XVIII.

There exists an interesting class of substituted ferrocenes in which the two cyclopentadienyl rings are bridged by the same substituent. In some of

⁶ See Volume 2 of *Advances in Organometallic Chemistry*, chapter 7 by Birmingham.

TABLE XVII

SUMMARY OF MAGNETIC RESONANCE DATA FOR COMPOUNDS CONTAINING THE π -C₅H₅ GROUP

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References
<i>Subgroup IV</i>							
Cp ₂ TiMe ₂	1.5	Cp \sim 4.2	—	—	—	40 Mc/sec	283
	—	Me 10.3	—	—	—	$\delta_{\text{C}_5\text{H}_5\text{Me}} = 0$	
Cp ₂ TiMeCl	—	Cp 4.00	—	—	—	C ₆ H ₆ soln	24
	—	Me 9.00	—	—	—		
Cp ₄ Th	—	3.6	—	—	—	CDCl ₃	123
<i>Subgroup</i>							
Cp ₂ V (paramagnetic)	-0.026% (at 3750 gauss)	—	—	—	—	16 Mc/sec relative to protons in PhMe	218, 243
[Cp ₂ V(CO) ₂] ⁺ [V(CO) ₆] ⁻	1.48 (C ₆ H ₆)	\approx 4.11	—	—	—	Me ₂ CO soln	49
Cp ₂ TaH ₃	—	Cp 5.24	—	—	—	56.45 Mc/sec	142, 239
Cp ₂ TaH ₃	—	TaH ₃ 13.02	—	—	9.6	$\gamma_{\text{Cp-H}_3}$ not obs	
		11.63					
<i>Subgroup VI</i>							
Cp ₂ Cr (paramagnetic)	-0.029% (at 3750 gauss)	—	—	—	—	16 Mc/sec relative to protons in PhMe	218, 243
CpCr(CO) ₃ H	3.1 (C ₆ H ₅ Me)	\approx 5.8	—	—	—	40 Mc/sec	283
		H \approx 15.8	—	—	—		
CpCr(NO) ₂ Me	2.6	Cp \approx 5.3	—	—	—	40 Mc/sec	348
	(C ₆ H ₅ Me)	Me \approx 9.6	—	—	—		

TABLE XVII—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multiplicity	\mathcal{J} (cps)	Remarks	References
$\text{CpCr(NO)}_2\text{I}$		4.24	—	—	—		199a
$\text{CpCr(NO)}_2(\sigma\text{-C}_5\text{H}_5)$	0.0 (H_2O)	$\text{Cp} \approx 4.6$	—	—	—	40 Mc/sec	348
$[\text{CpCr(NO)}_2]_2$	—	4.82	—	—	—		199a
$\text{CpCr(NO)}_2(\sigma\text{-C}_5\text{H}_5)$	1.8 ($\text{C}_6\text{H}_5\text{Me}$)	$\text{Cp} \approx 4.5$	—	—	—		283
		$(\sigma\text{-C}_5\text{H}_5) \approx 3.2$	—	—	—		
$\text{CpCr(C}_7\text{H}_8\text{Me)}$	—	6.83	—	—	—		116
$\text{CpCr(C}_7\text{H}_7)$	—	6.28	—	—	—	CS_2 soln	198
		6.38	—	—	—	C_6H_6 soln	197
$\text{CpCr(C}_7\text{H}_7)$	—	6.90	—	—	—	C_6D_6 soln	115
$\text{CpCrC}_{10}\text{H}_{11}$	—	6.16	—	—	—		117
$\text{CpCrC}_{13}\text{H}_{15}$	—	6.37	—	—	—		117
$\text{CpCrC}_{10}\text{H}_9$	—	6.29	—	—	—		117
							133
$\text{CpCr(CO)}_2(\text{C}_5\text{H}_7)$	—	4.7	—	—	—	60 Mc/sec for C_5H_7 See Table XIV	132
Cp_2MoH_2	—	$\text{Cp } 5.64$	—	3	0.96		142
		$\text{H}_2 \text{ } 18.76$	—	—	—		
$\text{Cp}_2\text{MoH}_3^+$	—	$\text{Cp } 4.38$	—	—	—		142
		$\text{H}_3 \text{ } 16.08$	—	—	—		
$\text{CpMo}(\sigma\text{-C}_5\text{H}_5)_3$	2.87 (C_6H_6)	$\text{Cp} \approx 5.5$	—	—	—		119
	3.4, 6.0	$\text{C}_5\text{H}_5 \approx 6.0, 8.6$	—	—	—		
$\text{CpMo(CO)}_3\text{H}$	2.5 (toluene)	$\text{Cp} \approx 5.4$	—	—	—	40 Mc/sec	283
		$\text{H} \approx 15.5$	—	—	—		
$\text{CpMo(CO)}_3\text{Me}$	2.6 (toluene)	$\text{Cp} \approx 5.3$	—	—	—	40 Mc/sec	283
		$\text{Me} \approx 9.6$	—	—	—		

CpMo(CO) ₃ C ₂ H ₅	-0.7 (H ₂ O)	Cp ≈ 5.3	—	—	—	C ₆ H ₁₂ soln	348
CpMo(CO) ₃ Et	2.5 (toluene)	Cp ≈ 5.2	—	—	—	40 Mc/sec	283
		Et ≈ 8.7	—	—	—		
CpMo(CO) ₃ i-Pr	2.5 (toluene)	Cp ≈ 5.2	—	—	—	40 Mc/sec	283
		Me ≈ 8.2	—	—	—		
[CpMo(CO) ₂ SMe] ₂	—	Cp 4.53, 4.70	—	—	—		358
		Me 8.13, 8.18	—	—	—		
CpMo(CO) ₂ C ₇ H ₇	—	Cp 5.21	5	—	—	CS ₂	197
		C ₇ H ₇ 4.93	7	—	—		
[CpMo(SMe) ₂] ₂	—	Cp 4.43	—	—	—		191
		Me 8.74	—	—	—		
CpMo(CO) ₃ COEt	—	Cp 5.41	—	—	—		240
		CH ₂ 7.82	—	—	—		
		CH ₃ 8.98	—	—	—		
CpMo(CO) ₃ σ-C ₃ H ₅	—	Cp 4.89	—	—	—	Neat liquid	69
CpMo(CO) ₂ π-C ₃ H ₅	—	Cp 5.26	—	—	—	C ₆ H ₆ + CS ₂	69
[CpMo(CO) ₃ C ₃ H ₅]PF ₆	—	4.05	—	—	—	Liq. SO ₂	69
[CpMo(CO) ₃ C ₃ H ₅ D]PF ₆	—	4.05	—	—	—	Liq. SO ₂	69
CpMoO ₂ Cl	—	3.40	—	—	—	CS ₂	69
[CpMo(CO) ₂ AsMe ₂] ₂	—	Cp 4.69	—	—	—		161
		Me 8.46	—	—	—		
[CpMo(CO) ₃] ₂ Hg	—	4.57	—	—	—	CHCl ₃	161
[CpMo(CO) ₂ PMe ₂] ₂	—	Cp 4.73	—	3	0.8	CDCl ₃	161
		Me 8.33	—	3	4.5		
[Cp ₂ Mo ₂ (CO) ₄ H]PMe ₂	—	Cp 5.31	10	2	0.3	C ₆ H ₆	161
		Me 8.38	6	2 × 2	9.9		
		H 21.73	—	2	36.6		
[CpMo(CO) ₃] ₂ H ⁺	—	Cp 4.28	—	—	—	98% H ₂ SO ₄	86
		H 30.99	—	—	—	56.45 Mc/sec	
[Cp ₂ MoW(CO) ₆]H ⁺	—	Cp ≈ 4.20	—	—	γ _{WH} = 38	98% H ₂ SO ₄	86
		H 32.88	—	—	—	56.45 Mc/sec	

TABLE XVII—*continued*

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Rela- tive Inten- sity	Multi- plicity	γ (cps)	Remarks	References
Cp_2WH_2	—	Cp 5.76 H ₂ 22.28	—	3	0.75		142
Cp_2WH_3^+	—	Cp 4.39 H(A ₂ B) 16.44, 16.08	—	—	—		142
$\text{CpW}(\text{CO})_3\text{H}$	2.4 (toluene)	Cp \approx 5.1 H 17.4	—	—	—	40 Mc/sec	283
$\text{CpW}(\text{CO})_3\text{H}_2^+$	—	Cp 4.03 H 11.93	—	—	—	56.45 Mc/sec	86
$[\text{CpW}(\text{CO})_3]_2\text{H}^+$	—	Cp 4.20 H 34.77	—	—	—	$\text{BF}_3 \cdot \text{H}_2\text{O} - \text{CF}_3\text{COOH}$ H ₂ SO ₄ ; 56.45 Mc/sec	86
$[\text{CpW}(\text{CO})_3]_2\text{H}^+\text{PF}_6^-$	—	Cp 4.10 H 34.8	—	—	38.6	56.45 Mc/sec	86
$[\text{CpW}(\text{CO})_3]_2\text{HgH}^+$	—	Cp 3.99 H 11.95	—	—	—	Liq. SO ₂ 56.45 Mc/sec	86
$[\text{CpW}(\text{CO})_2\text{SMe}]_2$	—	Cp 4.51 Me 8.11	5 3	—	—	$\text{BF}_3 \cdot \text{H}_2\text{O}$	358
$\text{CpW}(\text{CO})_3\text{COEt}$	—	Cp 5.41 CH ₂ 7.82 CH ₃ 8.98	—	—	—		240
$\text{CpW}(\text{CO})_3\sigma\text{-C}_3\text{H}_5$	—	4.75	—	—	—	C_6H_{12}	150
$\text{CpW}(\text{CO})_2\pi\text{-C}_3\text{H}_5$	—	5.37	—	—	—	C_6H_6	150
$[\text{CpW}(\text{CO})_3\text{C}_3\text{H}_6]\text{PF}_6$	—	4.01	—	—	—		150
$\text{CpW}(\text{CO})_3i\text{-Pr}$	—	Cp 5.41	—	—	—	C_6H_6	150
$[\text{CpW}(\text{CO})_2\text{PMe}_2]_2$	—	Cp 4.61 Me 8.13	—	3	0.4		161
			—	3	4.4		

CpW(CO) ₃ Me	2.5 (toluene)	Cp ≈ 5.2 Me ≈ 9.7	—	—	—	40 Mc/sec	283
CpW(CO) ₃ Et	2.5 (toluene)	Cp ≈ 5.2 Et ≈ 8.5	—	—	—	40 Mc/sec	283
CpW(CO) ₃ CF ₂ CF ₂ H	—	Cp 4.37 H 4.71	—	—	—		358
<i>Subgroup VII</i>							
Cp ₂ Mn (paramagnetic)	+0.012% (at 3750 gauss)	—	—	—	—	16 Mc/sec, relative to toluene	
CpMn(CO) ₃	—0.65 (H ₂ O)	≈ 5.3	—	—	—	40 Mc/sec, C ₆ H ₁₂	348
CpMn(CO) ₃	3.1 (toluene)	≈ 5.8	—	—	—	40 Mc/sec	283
[CpMn(CO) ₂ NO]PF ₆	—	3.86	—	—	—	Me ₂ CO	199
[CpMnCO(NO)] ₂	—	≈ 5.0	—	—	—	CCl ₄	199
		≈ 5.6	—	—	—	C ₆ H ₆	
Cp ₆ Mn ₆ (NO) ₈	—	4.94	—	—	—	CCl ₄	199
CpMn(NO) ₃ MnCpσ-C ₅ H ₅	—	Cp 4.7 σ-C ₅ H ₅ 5.6	—	—	—	Broad resonances	199
CpMn(C ₇ H ₈)(CO) ₂	—	6.61	—	—	—		131a
CpMn(CO) ₂ (CCF ₃) ₂	—	5.2	—	—	—		32
[CpMnC ₇ H ₈ Me]PF ₆	—	5.61	—	—	—		116
(Cp ₂ Tc) ₂	—	5.61	—	—	—	40 Mc/sec THF + toluene	177
[Cp ₂ Tc] ₂ H ⁺	—	4.60	—	—	—	40 Mc/sec, THF/H ₂ O	177
						No high-field resonance obsd	
Cp ₂ ReH	3.1 (toluene)	Cp ≈ 5.8 H 23.2	—	—	—	40 Mc/sec	283, 375
Cp ₂ ReH	1.1 (H ₂ O)	Cp ≈ 6 H ≈ 23.5	—	2	1.05	C ₆ H ₆ or CS ₂	147
Cp ₂ ReH	—	Cp 5.69 H 23.4	—	2	1.17	40 Mc/sec	177
Cp ₂ ReD	1.1 (H ₂ O)	≈ 6	—	—	—	Toluene	
						40 Mc/sec, C ₆ H ₆	147

TABLE XVII—*continued*

Compound	δ (ppm)	τ [$\delta(\text{CH}_3)_4\text{Si} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
$\text{Cp}_2\text{ReH}_2^+\text{Cl}^-$	-0.8 (H_2O)	$\text{Cp} \approx 4.4$	—	—	—	H_2O	147
		H_2 23.7	—	—	—		
$\text{Cp}_2\text{ReH}_2^+\text{Cl}^-$	—	Cp 4.54	—	3	—	$\text{H}_2\text{O}/\text{THF}$, 40 Mc/sec	177
		H_2 23.9	—	—	—		
$\text{Cp}_2\text{ReD}_2^+\text{Cl}^-$	0.8 (H_2O)	≈ 6.0	—	—	—	40 Mc/sec	147
$\text{CpRe}(\text{CO})_2(\text{C}_5\text{H}_5)$	—	4.4	—	—	—		148, 152
$\text{CpRe}(\text{CO})_2(\text{C}_5\text{H}_5)$	—	3.9	—	—	—		148, 152
<i>Subgroup VIII</i>							
Cp_2Fe	-1.2 (H_2O)	≈ 5.8	—	—	—	40 Mc/sec, C_6H_{12}	348
Cp_2Fe	3.200 (C_6H_6)	≈ 5.9	—	—	—	60 Mc/sec, THF	129
Cp_2Fe		6.00	—	—	—	10% in C_6H_6	302
Cp_2Fe		5.85	—	—	—	10% in CDCl_3	302
Cp_2Fe		5.86	—	—	—	10% in CDCl_3	296
Cp_2Fe	3.1 (toluene)	≈ 5.8	—	—	—	40 Mc/sec	283
Cp_2Fe		5.958	—	—	—	CCl_4	354
Cp_2FeH^+		Cp 4.99	—	2	1.2		76
		H 12.07	—	—	—		
		(broad)	—	—	—		
$[\text{CpFe}(\text{CO})_2]_2\text{H}^+$	—	Cp 4.76	—	—	—	Several solvents	86
		H 36.30	—	1	—	56.45 Mc/sec	
$\text{CpFe}(\text{CO})_2\text{Me}$	3.0 (toluene)	$\text{Cp} \approx 5.7$	—	—	—	40 Mc/sec	283
		$\text{Me} \approx 9.9$	—	—	—		
$\text{CpFe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$	2.1 (toluene)	$\text{Cp} \approx 4.8$	—	—	—	40 Mc/sec	283
$\text{CpFe}(\text{CO})_2(\sigma\text{-C}_5\text{H}_5)$	-0.3 (H_2O)	$\text{Cp} \approx 4.9$	—	—	—		348

CpFe(CO) ₂ σ-C ₃ H ₅	—	5.45	—	—	—	40 Mc/sec	143
CpFe(CO) ₂ σ-C ₃ H ₃	—	Cp 5.10	—	—	—	τ _{C₃H₃} = 7.93, 5.31, 3.84	143
[CpFe(CO) ₂ C ₃ H ₄] ⁺ SbCl ₆ ⁻	—	C ₃ H ₃ 8.2	—	—	—		17
[CpFe(CO) ₂ (CH ₂) ₂] ₂	—	4.02	—	—	—	Other band at 7.65–7.75	17
		Cp 5.16	5	—	—		192
		CH ₂ 7.17	4	3	—		
		CH ₂ 8.64	4	5	—		
[CpFe(CO) ₂] ₂ (CH ₂) ₃	—	Cp 5.18	10	1	—		192
		CH ₂ 7.17	4	3	7		
		CH ₂ 8.42	2	5	—		
CpFe(CO) ₂ (CH ₂) ₃ COFe(CO) ₂ Cp	—	Cp(a) 5.27	5	—	—		192
(a)	(b)	Cp(b) 5.17	5	—	—		
		CH ₂ 7.09	2	3	—		
		CH ₂ 8.61	4	M	—		
CpFe(CO) ₂ COMe	—	Cp 5.13	5	—	—		192
		Me 7.53	3	—	—		
CpFe(CO) ₂ CONMe ₂	—	Cp 5.12	5	—	—		192
		Me 7.02	6	—	—		
CpFe(CO) ₂ CONEt ₂	—	Cp 5.15	5	—	—		192
		CH ₂ 6.57	4	7	—		
		CH ₃ 8.91	6	—	—		
CpFeC ₄ H ₄ N	—	Cp 5.85	5	—	—		199a
		CH 4.74	2	—	—		
		CH 5.55	2	—	—		
CpFe(CO) ₂ COEt	—	Cp 5.56	—	—	—		240
		CH ₂ 7.28	—	—	—		
		CH ₃ 9.10	—	—	—		
[CpFe(CO) ₂]CO(CF ₂) ₃ CO[(Co) ₂ FeCp]		5.04	—	—	—		192
[CpFe(CO) ₂ σ-C ₃ H ₅]PF ₆		4.41	—	—	—		146
CpFeC ₅ H ₄ HgCl		5.55	—	—	—	o-C ₆ H ₄ Cl ₂ , 94° C	295
		5.94	—	—	—	Ph ₂ O, 94° C	

TABLE XVII—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
[CpFeC ₅ H ₄] ₂ Hg		5.37	—	—	—	o-C ₆ H ₄ Cl ₂ , 94° C	295
		5.82	—	—	—	Ph ₂ O, 94° C	
		5.90	—	—	—	PhNO ₂ , 94° C	
CpFeC ₅ H ₄ I	—	5.92	—	—	—	CDCl ₃	295
CpFeC ₅ H ₄ CO ₂ Me	—	5.81	—	—	—	CDCl ₃	295
[CpFeC ₅ H ₄] ₂	—	6.03	—	—	—		138
CpFe(CO) ₂ Et	—	5.40	—	—	—	Neat liquid	144
CpFe(CO) ₂ n-Pr	—	5.41	—	—	—	Neat liquid	144
CpFe(CO) ₂ i-Pr	—	5.42	—	—	—	Neat liquid	144
CpFe(CO) ₂ CDMe ₂	—	5.41	—	—	—	Neat liquid	144
CpFeC ₅ H ₄ Me	—	6.03	—	—	—	10% in C ₆ H ₆	302
CpFeC ₅ H ₄ COMe	—	5.82	—	—	—	10% in CDCl ₃	296
CpFeC ₅ H ₄ COPh	—	5.42	—	—	—	10% in CDCl ₃	296
<i>trans</i> -[CpFe(CO)AsMe ₂] ₂	—	Cp 5.90	—	—	—		162
		Me 8.65	—	—	—		
<i>cis</i> -[CpFe(CO)AsMe ₂] ₂	—	Cp 5.93	—	—	—		162
		Me 8.54, 8.77	—	—	—		
<i>trans</i> -[CpFe(CO)PMe ₂] ₂	—	Cp 5.84	5	3	1.1		162
		Me 8.44	6	3	5.4		
<i>cis</i> -[CpFe(CO)PMe ₂] ₂	—	Cp 5.85	5	3	1.0		162
		Me 8.30, 8.53	3, 3	3	5.3, 5.9		
Cp ₂ Fe ₂ (CO) ₂ HPMe ₂	—	Cp 5.64	—	—	1.2		162
		Me 8.01, 8.20	—	—	6.5		
		H 28.73	—	—	43.5		

<i>trans</i> -[CpFe(CO)PPh ₂] ₂	—	Cp 6.13 Ph 2.45, 2.8	—	3	1.2		162
<i>cis</i> -[CpFe(CO)PPh ₂] ₂	—	Cp 6.01 Ph 2.7	—	3	1.0		162
Cp ₂ Fe ₂ (CO) ₂ HPPPh ₂	—	Cp 5.80 Ph 2.5, 2.83 H 28.67	—	2	1.3		162
[CpFe(CO) ₂ (C ₂ H ₅ Me)] ⁺ ClO ₄ ⁻	—	4.65	—	—	—	40 Mc/sec, liq. SO ₂	143
[CpFe(CO) ₂ (C ₂ H ₅ CH ₂ D)] ⁺ ClO ₄ ⁻	—	4.38	—	—	—	40 Mc/sec, liq. SO ₂	143
[CpFe(CO) ₂ (C ₂ H ₅ Et)] ⁺ ClO ₄ ⁻	—	4.36	—	—	—	40 Mc/sec, liq. SO ₂	143
[CpFe(CO) ₂ (C ₂ H ₅ C ₂ H ₄ D)] ⁺ ClO ₄ ⁻	—	4.41	—	—	—	40 Mc/sec, liq. SO ₂	143
[CpFe(CO)SMe] ₂	—	5.77	—	—	—	τ _{Me} = 8.68	205
CpFe(CO)(π-C ₃ H ₅)	—	5.94	—	—	—	40 Mc/sec	143
CpFeC ₆ H ₇	—	5.93	—	—	—	56.45 Mc/sec	181
						Benzene soln	
CpFeC ₆ H ₆ D	—	5.82	—	—	—	56.45 Mc/sec CCl ₄ soln	181
CpFe(C ₆ H ₆ ·C ₆ H ₅)	—	5.7	—	—	—	56.45 Mc/sec CCl ₄ soln	181
1,1-Diferrocenylethane	—	5.86	—	—	—		304
2,3-Diferrocenyl-2,3-dimethyl- butane	—	5.94	—	—	—		304
[CpFeMn(CO) ₇]H ⁺	—	Cp 4.68 H 38.07	—	—	—	56.45 Mc/sec	86
			—	1	—	H ₂ SO ₄ soln	
[CpFeMn(CO) ₇]D ⁺ PF ₆ ⁻	—	4.55	—	—	—	56.45 Mc/sec, liq. SO ₂	86
Cp ₂ Ru	2.7 (toluene)	≈ 5.4	—	—	—	40 Mc/sec, C ₆ H ₁₂	283
Cp ₂ Ru	2.805 (C ₆ H ₆)	≈ 5.4	—	—	—	60 Mc/sec, C ₄ H ₈ O	129
Cp ₂ Ru	—	5.958	—	—	—	CCl ₄	356
Cp ₂ Ru	—	5.45	—	—	—	10% in CDCl ₃	296
CpRu(CO) ₂ COEt	—	Cp 4.69 CH ₂ 7.80 CH ₃ 8.99	—	—	—		240
CpRuC ₅ H ₄ COMe	—	5.42	—	—	—	10% in CDCl ₃	296
CpRuC ₅ H ₄ COPh	—	5.39	—	—	—	10% in CDCl ₃	296

TABLE XVII—continued

Compound	δ (ppm)	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multiplicity	\mathcal{J} (cps)	Remarks	References
CpRuC ₅ H ₃ (COPh) ₂	—	5.23	—	—	—	10% in CDCl ₃	296
Cp ₂ RuH ⁺	—	Cp 4.67 H 17.2	—	—	—	BF ₃ · H ₂ O soln 40 Mc/sec	76
[Cp ₂ Ru(CO) ₂] ⁺ H ⁺	—	Cp 4.48 H 28.58	—	—	—	56.45 Mc/sec	86
Cp ₂ Os	—	5.29	—	—	—	CDCl ₃	354
Cp ₂ Os	2.696 (C ₆ H ₆)	≈ 5.3	—	—	—	THF	129
Cp ₂ Os	—	5.30	—	—	—	10% in CDCl ₃	296
CpOsC ₅ H ₄ COMe	—	5.21	—	—	—	10% in CDCl ₃	296
CpOsC ₅ H ₄ COPh	—	5.18	—	—	—	10% in CDCl ₃	296
[CpOs(CO) ₂] ₂	—	4.7	—	—	—	Et ₂ O soln	114
Cp ₂ Co (paramagnetic)	+ 0.004% (at 3750 gauss)	—	—	—	—	16 Mc/sec relative to toluene	243 218
CpCoC ₅ H ₆	—	5.41	—	—	—	40 and 60 Mc/sec	148
CpCoC ₈ H ₁₀	—	5.34	—	—	—		247
CpCoC ₈ H ₈	—	5.3	—	—	—	CCl ₄	87
		5.8	—	—	—	CDCl ₃	131
		5.33	—	—	—	CS ₂ , 40 Mc/sec	204
		5.3	—	—	—	CCl ₄ , 56.45 Mc/sec	86
CpCoBr(C ₃ H ₅)	—	4.06	—	—	—		166
CpCoI(C ₃ H ₅)	—	3.93	—	—	—		166
CpCoC ₅ H ₅ D	—	5.41	—	—	—	40 Mc/sec	148
CpCo(C ₅ H ₅ Me)	—	5.39	—	—	—	40 Mc/sec	148
CpCo(C ₅ H ₅ CCl ₃)	—	5.25	—	—	—	40 Mc/sec	148

CpCo(C ₅ H ₅ CHCl ₂)	—	5.25	—	—	—	40 Mc/sec	148
(CpCo) ₂ C ₂ F ₄	—	4.62	—	—	—		173
(Cp ₂ Co) ₂ C ₅ H ₄	—	5.27	—	—	—		131
CpCo(C ₅ H ₅ C ₉ H ₇)	—	5.3	—	—	—		131
CpCoC ₈ H ₈	—	5.37	—	—	—		204
(CpCo) ₂ C ₉ H ₈	—	5.38	—	—	—	CS ₂ , 60 Mc/sec	204
CpCoC ₈ H ₁₀	—	5.55	—	—	—	CS ₂ , 60 Mc/sec	204
CpCo(C ₁₄ H ₁₄ F ₆)	—	5.37	—	—	—	60 Mc/sec	190
CpCo(CO) ₂	—	5.08	—	—	—	40 and 56.45 Mc/sec	70
[CpCoSMe] ₂	—	Cp 5.18 Me 7.48	—	—	—	60 Mc/sec	205
CpCo(CO)C ₄ F ₈	—	4.57	—	—	—	CDCl ₃ , 60 Mc/sec	70
CpCo(CO)(C ₃ H ₇)I	—	4.35	—	—	—	40 and 56.45 Mc/sec	70
Cp ₂ RhC ₈ H ₈	—	4.85	—	—	$\gamma_{\text{RhCp}} = 0.71$	56.45 Mc/sec	86
Cp ₂ RhC ₈ H ₈	—	5.19	—	—	—		33a
Cp ₂ RhC ₈ H ₈	—	4.85	—	—	$\gamma_{\text{RhH}} = 0.71$	CCl ₄	87
CpRh(1- <i>exo</i> -C ₅ H ₅ Ph)	—	4.81	—	2	—	CCl ₄ soln	13
[CpRh(C ₅ H ₄ Ph)]I ₃	—	4.04	—	2	—	Me ₂ CO soln	13
CpRh(1- <i>exo</i> -C ₅ H ₅ C ₅ H ₅)	—	4.96	—	2	—	C ₆ D ₆	13
CpRh(C ₂ H ₄) ₂	—	4.92	—	—	—		193
CpRhC ₅ H ₈	—	4.87	—	—	$\gamma_{\text{RhCp}} = 1.0$	40 and 60 Mc/sec	86
CpIr(CO) ₂	—	5.81	—	—	—	C ₆ H ₆	118
Cp ₂ Ni (paramagnetic)	+0.032% (at 3750 gauss)	—	—	—	—	16 Mc/sec relative to toluene	218, 242
CpNiC ₃ H ₅	—	4.21	—	—	—		238
CpNiC ₅ H ₇	—	4.78	—	—	—		99
		4.72	—	—	—		125
CpNiC ₁₃ H ₁₇	—	5.06	—	—	—		193
[CpNiPPh ₂] ₂	—	Cp 5.16 Ph 2.2, 2.75	—	3	0.6	CDCl ₃	161
[CpNiPMe ₂] ₂	—	Cp 5.13 Me 8.67	5	1	—		161
			6	3	6.6		

TABLE XVII—continued

Compound	δ (ppm)	τ [$\delta(\text{CH}_3)_4\text{Si} = 10$]	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References
[CpNiAsMe ₂] ₂	—	Cp 5.10 Me 8.79	5 6	— —	— —		161
CpNiC ₇ H ₅ F ₄	—	4.75	—	—	—		235
CpNiC ₇ H ₅ F ₃ Cl	—	4.78	—	—	—		235
CpNiC ₁₁ H ₁₁ O ₃	—	4.76	—	—	—		98
CpNiC ₁₃ H ₁₇	—	4.95	—	—	—		193
CpNiNO	2.2 (toluene)	4.9	—	—	—	40 Mc/sec	283
CpNiNO	-0.4 (H ₂ O)	≈ 5.0	—	—	—	C ₆ H ₆ soln	348
CpPdC ₃ H ₅	—	4.14	—	—	—		337
CpPdC ₃ H ₅	—	3.5	—	—	—		238
CpPdC ₆ H ₉	—	4.35	—	—	—		337
CpPd(C ₃ H ₄ CMe ₂ OMe)	—	4.38	—	—	—	CCl ₄ soln	306
CpPd(C ₄ H ₆ CMe ₂ OMe)	—	4.40	—	—	—	CCl ₄ soln	306
CpPd(C ₄ H ₆ CH ₂ OMe)	—	4.45	—	—	—	CCl ₄ soln	306
CpPd(Me ₂ C ₃ H ₂ CMe ₂ OMe)	—	4.50	—	—	—	CCl ₄ soln	306
CpPd(C ₄ H ₆ CH:CMe ₂)	—	4.51	—	—	—	CCl ₄ soln	306
CpPtC ₃ H ₅	—	4.25	—	—	$\gamma_{\text{PtCp}} = 11$		337
CpPt(CO)I	—	4.87	—	—	18.5	$\gamma_{\text{Pt}^{103}\text{H}}$	132a
(CpPtCO) ₂	—	Cp 4.50	—	—	6, 13.7	γ_{PtH} and γ_{PtPtH}	132a
CpFe(CO) ₂ σ -C ₄ H ₇	—	5.44	—	—	—	40 Mc/sec	143
						$\tau_{\text{C}_4\text{H}_7} = 8.43, 7.88, 4.57$	
CpFeC ₉ H ₇	—	6.38	—	—	—		199a
CpFeC ₉ H ₁₁	—	6.16	—	—	—		199a

TABLE XVIII

SUMMARY OF MAGNETIC RESONANCE DATA FOR SUBSTITUTED π -CYCLOPENTADIENYL DERIVATIVES, MISCELLANEOUS OTHER COMPLEXES CONTAINING THE π -(C₅)M SYSTEM, AND SOME OF THE FREE OLEFINS

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multiplicity	γ (cps)	Remarks	References
C ₅ H ₅ CH ₃ , methycyclopentadiene ^a						
CH ₃	~ 8.0	—	—	—	40 Mc/sec $\delta_{\text{H}_2\text{O}} = 0$ $\delta_{\text{C}_4\text{H}_4} = 3.9$	348
>CH	~ 3.5	—	—	—		
CHCH ₃	~ 7.2	—	—	—		
(C ₅ H ₄ CH ₃) ₂ Fe ^b						
CH ₃	~ 8.0	—	—	—		
C ₅ H ₄	~ 6.0	—	—	—		
(C ₅ H ₄ CH ₃) ₂ Fe ^c						
CH ₃	~ 8.1	—	—	—	$\delta_{\text{C}_6\text{H}_5\text{CH}_3} = 0$	283
C ₅ H ₄	~ 5.7	—	—	—		
(C ₅ H ₄ CH ₃)Mn(CO) ₃ ^d						
CH ₃	~ 8.1	—	—	—	40 Mc/sec $\delta_{\text{H}_2\text{O}} = 0$ $\delta_{\text{C}_4\text{H}_4} = 3.9$	348
C ₅ H ₄	~ 5.5	—	—	—		
(C ₅ H ₄ CH ₃)Ni(C ₅ H ₆ CH ₃)						
CH ₃	7.99	—	—	—	For (C ₅ H ₆ CH ₃) group see Table XV	125
C ₅ H ₄	4.90	—	—	—		
1,1-Diferrocenylethane (C ₅ H ₅ FeC ₅ H ₄) ₂ CHCH ₃						
C ₅ H ₅ } C ₅ H ₄ }	5.86	—	—	—		304
>CH	6.58	—	—	—		
CH ₃	8.86	—	—	—		

TABLE XVIII—continued

Compound	p.p.m.	τ [$\delta_{(\text{CH}_4)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
2,3-Diferrocenyl-2,3-dimethylbutane							
C_5H_4		5.86	—	1	—		303
C_5H_5		5.94	—	1	—		
CH_3		8.69	—	1	—		
1,1'-(Diisopropyl)ferrocene							
C_5H_4		5.79	—	—	—		303
CH_3		8.86	—	2	—		
>CH		7.36	—	m	—		
1,1'-($\alpha,\alpha,\beta,\beta$ -Tetramethyldimethylene)ferrocene							
$\boxed{\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{C}(\text{CH}_3)_2}$							
C_5H_4		$\left\{ \begin{array}{l} 5.37 \\ 6.11 \end{array} \right.$	$\left\{ \begin{array}{l} \text{—} \\ \text{—} \end{array} \right.$	$\left\{ \begin{array}{l} 3 \\ 3 \end{array} \right.$	1.6		303
1,1'-(Trimethylene)ferrocene							
$\boxed{\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 \cdot (\text{CH}_2)_3}$							
C_5H_4		6.05	—	1	—	CDCl ₃ , 60 Mc/sec	303
CH_2		8.05	—	—	—		310
							309
1,1'-(β,β -Dimethyltrimethylene)ferrocene							
$\boxed{\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}(\text{CH}_3)_2 \cdot \text{CH}_2}$						60 Mc/sec	309
C_5H_4		$\left\{ \begin{array}{l} 5.97 \\ 6.06 \end{array} \right.$	$\left\{ \begin{array}{l} \text{—} \\ \text{—} \end{array} \right.$	$\left\{ \begin{array}{l} 3 \\ 3 \end{array} \right.$	2		

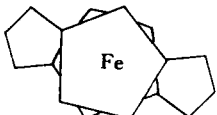
1,1'-(Dimethyleneoxy)ferrocene $\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2$	5.88	—	1	—		303
1,1'-(Tetramethylene)ferrocene ^f $\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4 \cdot (\text{CH}_2)_4$	~ 6	—	—	—	CDCl ₃ soln, 60 Mc/sec	309
$\alpha\text{-CH}_2$	7.58	—	—	—		
$\beta\text{-CH}_2$	8.17	—	—	—		
1,1'-3,3'-bis-(Trimethylene)ferrocene 	C_5H_3	6.13	—	—	CDCl ₃ soln, 60 Mc/sec	309
>CH_2	8.10	—	b	—		
$\text{C}_6\text{H}_7\text{Mo}(\text{C}_6\text{H}_9)(\text{CO})_2$	4.0	(1)	—	—	This compound may also exist in isomeric form, as $(\text{C}_6\text{H}_8)_2\text{Mo}(\text{CO})_2$; see Table XV	132
	5.35	(3)	—	—		
	7.05	(2)	—	—		
	8.2	(6)	—	—		
	9.1	(4)	—	—		
$\text{C}_6\text{H}_7\text{Mn}(\text{CO})_3$ (see text)						
H_a	4.80	(1)	3×3	$\mathcal{J}_{ab} = 5.1$ $\mathcal{J}_{ac} = 1.2$	C_6H_6 soln; 40 and 56.45 Mc/sec; also observed in	378
H_b	5.84	(2)	~ 3	$\mathcal{J}_{bc} = 6.5$	C_6H_{12} , CCl_4 , CHCl_3 ,	379
H_c	7.65	(3)	c	—	$(\text{CH}_3)_2\text{CO}$, and $(\text{CH}_3)_2\text{SO}$ solns	
>CH_2	$\left\{ \begin{array}{l} 7.75 \\ 8.44 \end{array} \right\}$	(2)	AB pair	$\mathcal{J}_{AB} = 11$		
$\text{C}_6\text{H}_6\text{DMn}(\text{CO})_3$						
H_a	4.83	Same as band for H_a in $\text{C}_6\text{H}_7\text{Mn}(\text{CO})_3$				379
H_b	5.84	(2)	3	$\left. \begin{array}{l} \mathcal{J}_{ab} \\ \mathcal{J}_{bc} \end{array} \right\} \simeq 5.5$	Other unassigned bands also reported	

TABLE XVIII—continued

Compound	p.p.m.	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References		
$\text{C}_6\text{H}_7\text{Fe}(\text{CO})_3\text{BF}_4$									
H_a		2.66	(1)	3	$\mathcal{J}_{ab} = 5.5$	SO_2 soln	181		
H_b		4.08	(2)	2×2	$\mathcal{J}_{bc} = 6.0$				
H_c		5.66	(2)	2×2	—				
$\text{>C} \begin{smallmatrix} \text{H}_A \\ \text{H} \end{smallmatrix}$		$\left\{ \begin{array}{l} 7.09 \\ 6.86 \end{array} \right.$	(1)	3×2	>CH_2 , AB pair $\mathcal{J}_{AB} = 15.0$ $\mathcal{J}_{Ac} = 6.5$				
$\text{>C} \begin{smallmatrix} \text{H} \\ \text{H}_B \end{smallmatrix}$		$\left\{ \begin{array}{l} 7.85 \\ 8.11 \end{array} \right.$	(1)	—	—				
$\text{C}_6\text{H}_7\text{FeC}_5\text{H}_5$									
H_a		4.31	(1)	3×3	$\mathcal{J}_{ab} = 5.6$ $\mathcal{J}_{ac} = 1.5$	56.45 Mc/sec C_6H_6 soln	181		
C_5H_5		5.93	(7)	—	—				
H_b									
>CH_2		7.46, 8.4	(4)	c	>CH_2 , AB pair $\mathcal{J}_{AB} = 12.0$				
H_c									
$\text{C}_6\text{H}_6\text{DFeC}_5\text{H}_5$									
H_a		4.01	(1)	3	$\mathcal{J}_{ab} = 4.8$	56.45 Mc/sec CCl_4 soln	181		
C_5H_5		5.82	(7)	—	—				
H_b									
H_c		7.46 to 8.7	(3)	c	—				
>CHD									



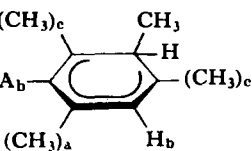
(C ₆ H ₇) ₂ Ru						C ₆ H ₆ soln This compound may also exist in isomeric form, as C ₆ H ₈ RuC ₆ H ₆ ; see Tables XV and XIX	181
H _a	4.91	(1)	3	$\mathcal{J}_{ab} = 5.0$			
H _b	5.63	(2)	2 × 2	—			
H _c	7.00	}	(4)	—	—		
CH ₂	7.09						
C ₆ H ₇ ReC ₆ H ₆							
H _a	4.13	(1)	3	$\mathcal{J}_{ab} = 5$		181	
H _b	5.10	(2)	2 × 2	$\mathcal{J}_{bc} = 5$			
C ₆ H ₆	5.35	(6)	—	—			
	5.96	}	(1)	AB pair	$\mathcal{J}_{ab} = 11.5$		
	6.00						
H _c	6.81	(2)	2 × 2	$\mathcal{J}_{bc} = 6$			
	7.48	(2)	"5"	$\mathcal{J}_{BC} = 5.5$			
Substituted Cyclohexadienyl complexes							
(C ₆ H ₆ ·φ)FeC ₅ H ₅							
φ	3.1	}	(5)	2	—	56.45 Mc/sec	181
	3.33			4	—		
H _a	4.2	(1)	"3"	$\mathcal{J}_{ab} = 5.0$		CCl ₄ soln	
C ₅ H ₅	5.7	(7)	—	—			
CHφ	6.51	(1)	3	$\mathcal{J}_{CH\phi-H_c} = 6.5$			
H _c	7.27	(2)	3				
(C ₆ H ₆ ·φ) ₂ Ru							
φ	3.0	(5)	—	—		56.45 Mc/sec	181
H _a	4.77	(1)	3	$\mathcal{J}_{ab} = 5.0$		CCl ₄ soln	
H _b	5.37	(2)	"3"	$\mathcal{J}_{bc} = 5.3$			
CHφ	6.6	}	(3)	c	—		
	to						
H _c	5.98						

TABLE XVIII—continued

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	J (cps)	Remarks	References
$(\text{C}_6\text{H}_6 \cdot \phi)\text{Mn}(\text{CO})_3$						
ϕ	$\left\{ \begin{array}{l} 2.75 \\ \text{to} \\ 3.35 \end{array} \right.$	$\left. \begin{array}{l} \\ \\ \end{array} \right\} (5)$	c	—	56.45 Mc/sec CCl_4 soln	181
H_a	4.33	(1)	3	$J_{ab} = 7.5$		
H_b	5.18	(2)	"3"	$J_{bc} = 9.5$		
$\text{CH}\phi$	6.27	(1)	"3"	5.5		
H_c	6.61	(2)	"3"	—		
$(\text{C}_6\text{H}_6 \cdot \text{CH}_3)\text{Mn}(\text{CO})_3$						
H_a	4.89	—	3	—	Two main isomers among several other products detected	377
$(\text{CH}_3)_b$	8-9	—	—	—		
H_c	4.16	—	—	—		
$\text{H}_{a'}$	4.96	—	—	—		
$\text{H}_{b'}$	5.57	—	—	—		
$[\text{C}_6\text{H}_3 \cdot (\text{CH}_3)_4]\text{Mn}(\text{CO})_3$						
	$(\text{CH}_3)_a$ H_b $(\text{CH}_3)_c$	$\left\{ \begin{array}{l} 4.95 \\ 5.8 \\ 7.7 \end{array} \right.$	—	—	56.45 and 40 Mc/sec Spectrum poorly resolved C_6H_6 soln	377
			—	—		
			—	—		

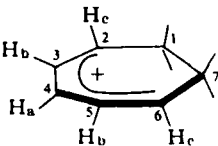
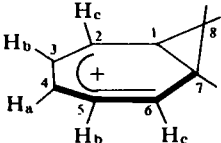
$(C_6H \cdot (CH_3)_6)Mn(CO)_3$							
$(CH_3)_a$	{	8.31	—	—	—	377	
$(CH_3)_b$		8.33	—	—	—		
$(CH_3)_c$		8.73	—	2	$J \approx 1$		
$>CH(CH_3)$		~ 8.2	—	2	$J \approx 6$		
<i>Seven-Membered Rings</i>							
$C_7H_7Fe(CO)^+_3$		4.20	—	—	—	BF_4^- salt/ SO_2 soln	
$(C_7H_8 \cdot H)^+Fe(CO)_3$						223a	
	H_a	3.03	(1)	3	$J_{ab} = 6.5$	H_2SO_4	85
	H_b	4.81	(2)	2×2	$J_{bc} = 9.9$		80
	H_c	5.15	(2)	b	—		
	$>CH_2$	{	~ 7.4	{ (4)	—	—	
			~ 8.2				
$(C_7H_8 \cdot D)^+Fe(CO)_3$							
H_a		2.96	(1)	3	Same coupling as above	D_2SO_4	86
H_b		4.07	(2)	2×2			
H_c		5.08	(2)	b	—		80
$>CH_2$	{	~ 7.4	(2)	c	—		
$>CHD$		~ 8.21	(1)	2×2	{ 16.5 7.5		
$(C_7H_9)Fe(CO)_2I$		3.1	(2)	—	—	$(CCl_3)_2CO$ soln	80
		6.1	(2)	—	—		
		7.7	(2)	—	—		
		8.5	(2)	—	—		

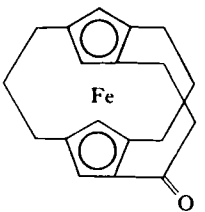
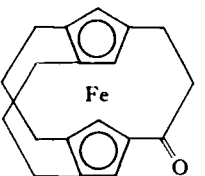
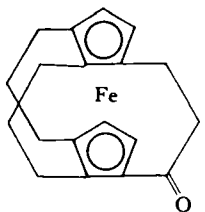
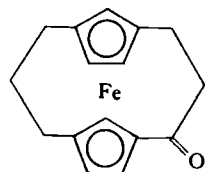
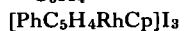
TABLE XVIII—continued

Compound		τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References	
$(\text{C}_8\text{H}_8 \cdot \text{H}^+)\text{Fe}(\text{CO})_3$		H_a $\text{H}_{b,c}$ $\text{H}_{1,7}$ $>\text{CH}_2$	2.26 4.62 4.62 { 8.65 f 8.47 f	(1) (4) (2) — —	5 b b c c	$\mathcal{J}_{ab}\mathcal{J}_{ac} \sim 3.8$ — — $\mathcal{J}_{AB} = 4.8$ + coupling to H_1, H_7	H_2SO_4 soln, 56.45 Mc/sec Spectrum identical in liquid SO_2	87 325
$(\text{C}_8\text{H}_8 \cdot \text{D}^+)\text{Fe}(\text{CO})_3$	H_a $\text{H}_{b,c}$ $\text{H}_{1,7}$ $>\text{CHD}$	2.18 4.55 7.44 8.59	— — — —	— — 2 3	— — } AB_2 $\mathcal{J}_{AB} = 7.96$	D_2SO_4	87	
Other Miscellaneous Groups								
$\text{C}_5\text{H}_4\text{CHNMe}_2\text{Cr}(\text{CO})_3$	C_5H_4	4.91	—	—	—		199b	
	CH	2.18	—	—	—			
	Me	6.54, 6.70	—	—	—			
$\text{C}_5\text{H}_4\text{C}(\text{NMe}_2)_2\text{Cr}(\text{CO})_3$	Me	6.66	—	—	—		199b	
	C_5H_4	—	—	—	—	Not observed		
$\text{C}_5\text{H}_4\text{CHNMe}_2\text{Mo}(\text{CO})_3$	C_5H_4	4.34	—	3	≈ 2		199b	
		4.49	—	3	≈ 2			
	Me	6.59, 6.70	—	—	—			
	CH	1.99	—	—	—			



Me

C_5H_4



C_5H_4

Ph

2

4

5

2'

4'

5'

4

5

4'

5'

3,5

3',5'

2

5

2'

5'

6.66

—

3.34, 3.85

2.61

5.54

5.38

6.06

5.86

5.77

6.42

5.52

6.14

5.74

6.25

5.67

5.97

6.30

5.66

6.62

5.88

—

—

4

5

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M

M

3

4

4

3

3

3

2

2

2

2

S

S

2

2

2

2

—

—

1.5

1.5

2.4

2.5

1.5

—

2.5

—

—

—

—

—

—

1.5

—

—

Not observed

$J_{2,4}$

$J_{2,5}$

$J_{4,5}$

$J_{4,5} = J_{4',5'}$

$J_{2,5} = J_{2',5'}$

$J_{4,5} = J_{4',5'}$

$2,5 = 2',5'$

199b

13

302

302

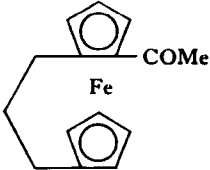
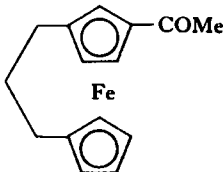
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302

Nuclear Magnetic Resonance

135

TABLE XVIII—continued

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References
(C₆H₄COMe)FeCp						
2,5	5.40	—	3	—	10% in C ₆ H ₆	302
3,4	5.94	—	3	—		
2',3',4',5'	6.18	—	1	—		
2,5	5.28	—	3	—	10% in CDCl ₃	302
3,4	5.54	—	3	—		
2',3',4',5'	5.80	—	1	—		
	3	5.46	—	3	10% in CDCl ₃	302
	4,2',3'	5.76	—	M		
	5	6.34	—	M		
	4'	6.14	—	—		
	5'	6.33	—	M		
	2,4	5.47	—	M		302
	5,3',4'	5.86	—	M		
	2',5'	6.17	—	Sb		

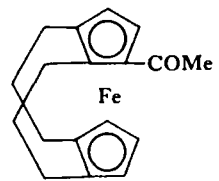
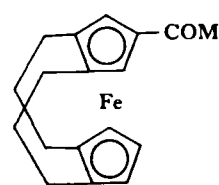
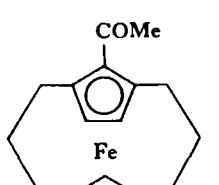
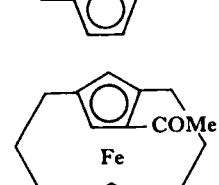
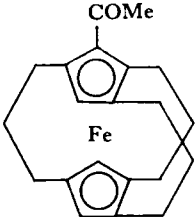
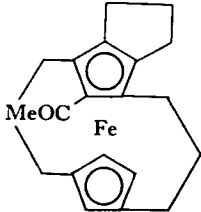
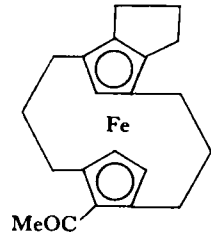
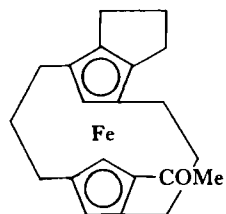
	4	5.65	—	2	—	$J_{4,5}$	302
	5	6.15	—	2	2.8		
	3',5'	6.40	—	M	—		
	4'	5.93	—	3	—		
	3	5.83	—	1	—		302
	5	5.80	—	—	—		
	3',4',5'	6.2	—	M	—		
	4,5	6.06	—	S	—		302
	2'	6.18	—	3(u)	—		
	4',5'	6.26	—	2(u)	—		
	2,4'	6.28	—	M	—	J_{25}	302
	5	5.83	—	2	1.7		
	2'	6.62	—	3(u)	—		
	5'	6.10	—	4(u)	—		

TABLE XVIII—continued

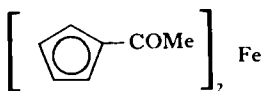
Compound		τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
	5	6.31	—	1	—	$\mathcal{J}_{3'5'}$	302
	3'	6.26	—	2	1.35		
	5'	6.54	—	2	—		
	2'	6.25	—	Sb	—	$\mathcal{J}_{2'4'}$	302
	4',5'	6.62	—	d(u)	1.4		
	2	6.25	—	S	—		302
	4',5'	6.38	—	S	—		



2	6.69	—	S	—
2'	6.22	—	2	1.7
5'	6.15	—	2	—

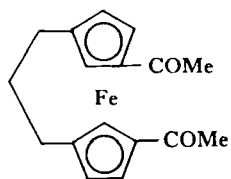
$J_{2'5'}$

302



2,5,2',5'	5.55	—	3	—
4,3,3',4'	6.07	—	3	—

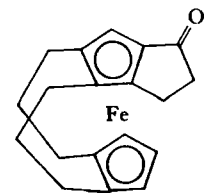
302



2,4,3',5'	5.65	—	M	1.59
5,2'	6.02	—	4	2.40

J_{25}
 J_{45}

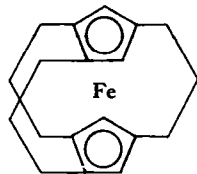
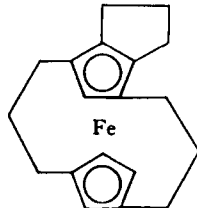
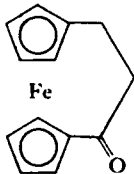
302



5	5.70	—	1	—
3'	6.10	—	4	—
4'	6.77	—	4	—
5'	5.99	—	3	—

302

TABLE XVIII—continued

Compound	τ [$\delta(\text{CH}_3)_2\text{Si} = 10$]	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References	
	6.37	—	S	—		302	
	6.44	—	Sb	—		302	
	2,5	5.38	—	M	—	10% in C_6H_6	302
	3,4	5.95	—	M	—		
	2',5'	5.78	—	M	—		
	3',4'	6.23	—	M	—		
		5.25	—	Sb	—	10% in CDCl_3	302
		5.68	—	Sb	—		
		5.45	—	Sb	—		
		6.04	—	Sb	—		

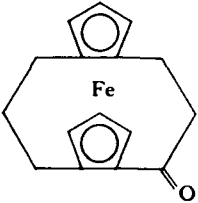
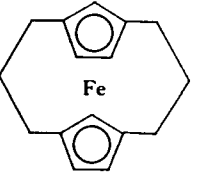
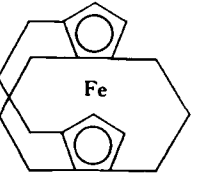
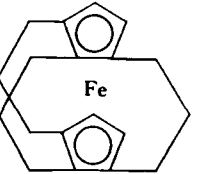
	3	5.67	—	3(u)	—	Unresolved 10% in C ₆ H ₆	302
	4,5,4'	6.11	—	M	—		
	3'	5.85	—	3(u)	—		
	5'	6.46	—	3(u)	—		
	3	5.30	—	3(u)	—	10% in CDCl ₃	302
	4,5,4'	5.86	—	M	—		
	3'	5.47	—	3(u)	—		
	5'	6.19	—	3(u)	—		
	H ₂ , 2'	6.43	—	3	1.5		302
	H ₄ , 4', 5, 5'	6.14	—	2	1.5		
	H ₄ , 4', 5, 5'	6.04	—	1	—		302

TABLE XVIII—continued

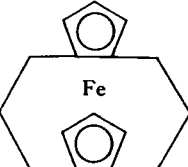
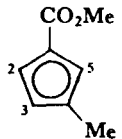
Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multiplicity	γ (cps)	Remarks	References
[C₅H₄CHNMe₂Fe(CO)₂]₂						
Isomer A C ₅ H ₄	≈ 4.9	8	C	—		199b
Me	7.78	12	1	—		
CH	6.93	2	1	—		
Isomer B C ₅ H ₄	4.73	4	—	Broad		
C ₅ H ₄	5.23	4	—	Broad		
Me	8.00	12	—	—		
CH	7.05	2	—	—		
[C₅H₄CHNMe₂Fe(CO)₂Me]₂						
C ₅ H ₄	5.3	8	C	—		199b
CH	6.54	2	1	—		
NMe	7.88	12	1	—		
FeMe	9.92	6	1	—		
[C₅H₄CMe₂CMe₂C₅H₄]Fe						
H _{2,5,2'5'}	6.01	—	3	—	10% in C ₆ H ₆	302
H _{3,3',4,4'}	5.46	—	3	—		
H _{2,5}	6.04	—	3	—	10% in CDCl ₃	302
H _{3,4}	5.37	—	3	—		
						
H _{3,3',5,5'}	6.20	—	2	2.5		302
H _{4,4'}	5.89	—	3	2.5		

TABLE XVIII—continued

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
$[\text{C}_5\text{H}_4\text{FeC}_5\text{H}_4\text{Hg}]_x$	5.77	—	—	—	167° C in PhNO_2	295
	5.50	—	—	—		
	6.00	—	—	—	184° C in PhNO_2	295
	5.73	—	—	—		
$(\text{C}_5\text{H}_4\text{I})\text{FeCp}$	5.67	1	3	—		295
	5.88	1	3	—		
$(\text{C}_5\text{H}_4\text{I})_2\text{Fe}$	5.68	1	3	—		295
	5.90	1	3	—		
$(\text{C}_5\text{H}_4\text{CO}_2\text{Me})\text{FeCp}$	5.21	2	3	—		295
	5.63	2	3	—		
	6.21	3	1	—		
<div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 10px;">$(\text{C}_5\text{H}_4\text{CO}_2\text{Me})\text{Fe}$</div>  </div>						
$\text{H}_{3,5,2',5'}$	5.31	4	—	—		26
$\text{H}_{3,4,3'}$	5.74	3	—	—		
ring Me	8.05	3	—	—		

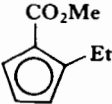
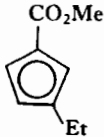
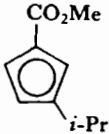
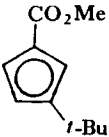
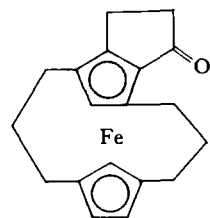
$(C_5H_4CO_2Me)Fe$ 	$H_{2,5}$ $H_{3,4}$ CH_2 of Et CH_3 of Et	5.33 5.78 7.36 8.80	3 4 2 3	— — — —	— — — —	26
$(C_5H_4CO_2Me)Fe$ 	$H_{2,5}$ $H_{3,4}$ CH_2 of Et CH_3 of Et	5.30 5.74 7.70 8.82	4 3 2 3	— — — —	— — — —	26
$(C_5H_4CO_2Me)Fe$ 	$H_{2,5}$ $H_{3,4}$ CH CH_3 of <i>i</i> -Pr	5.35 5.76 7.40 8.84	4 3 1 6	— — — —	— — — —	26

TABLE XVIII—continued

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Inten- sity	Multi- plicity	\mathcal{J} (cps)	Remarks	References
$(\text{C}_5\text{H}_4\text{CO}_2\text{Me})\text{Fe}$ 						
H _{2,5}	5.31	4	—	—		26
H _{3,4}	5.75	3	—	—		
CH ₃ of Bu	8.77	9	—	—		
$(\text{C}_5\text{H}_4\text{COMe})\text{FeCp}$	5.23	—	3	1.90	Triplet	296
	5.51	—	3	—		
$(\text{C}_5\text{H}_4\text{COMe})_2\text{Fe}$	5.23	—	3	1.91	Triplet	296
	5.49	—	3	—		
$\text{C}_5\text{H}_4\text{MeFeCp}$	6.07	—	—	—		302
	6.03	—	—	—		
$(\text{C}_5\text{H}_4\text{Me})_2\text{Fe}$	6.11	—	—	Broad		302
$[\text{C}_5\text{H}_4(\text{CH}_2)_3\text{C}_5\text{H}_4]\text{Fe}$						
H _{2,2',5,5'}	6.14	—	3	—	10% in C ₆ H ₆	302
H _{3,3',4,4'}	5.99	—	3	—		
H _{2,2',5,5'}	6.04	—	1	—	10% in CDCl ₃	302
H _{3,3',4,4'}	6.04	—	1	—		



H_{2,5'}
H_{2,4'}

6.25
6.70

— —
— —

M

302

(C₅H₄CO₂Me)₂Fe

5.18

2 3 —

295

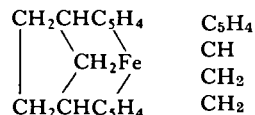
5.60

2 3 —

6.18

3 1 —

Me



C₅H₄
CH
CH₂
CH₂

5.85, 6.18

8 — —

67

7.13

2 — —

7.93

2 3 —

8.20

4 2 —

1,2-(α -Ketotetramethylene) ferrocene

H_{3,4}

5.91

— 2 —

302

H₅

5.13

— 3 —

Cp

6.12

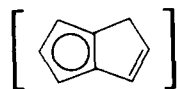
— 1 —

[C₅H₄FeCp]₂

5.82

1 3 2

138



Fe

Olefinic
C₅ ring
CH₂

5.68

1 3 —

3.92

4 — —

2 isomers

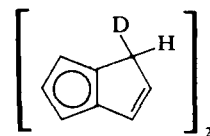
187

6.13

6 — —

7.33 and 7.50

4 — —



Fe

Olefinic
C₅ ring
CHD

3.92

4 — —

2 isomers

187

6.13

6 — —

7.33 and 7.50

2 — —

Broad

TABLE XVIII—*continued*

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Inten- sity	Multi- plicity	γ (cps)	Remarks	References
[C ₅ H ₄ CO ₂ Me]FeCp	5.28	1	—	—		26
	5.73	1	—	—		
[C ₅ H ₄ CO ₂ Me] ₂ Fe	5.20	1	—	—		26
	5.60	1	—	—		
[C ₅ H ₄ CO ϕ]Fe	5.08	—	3	1.93		296
	5.43	—	3	—		
[C ₅ H ₄ COPh]FeCp	5.10	—	3	1.91	Triplet	296
	5.43	—	3	—		

^a For CH₃, $\delta = 3.3$; >CH , $\delta = -1.1$; CHCH₃, $\delta = 2.5$ ppm.

^b For CH₃, $\delta = 3.35$; C₅H₄, $\delta = 1.4$ ppm.

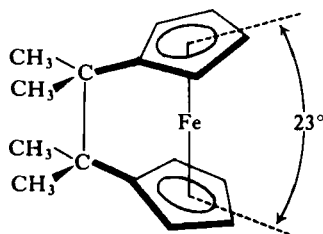
^c For CH₃, $\delta = 5.4$; C₅H₄, $\delta = 3.2$ ppm.

^d For CH₃, $\delta = 3.4$; C₅H₄, $\delta = 0.8$ ppm.

^e A variety of other substituted ferrocenes is presented in this work; see table above for additional bridging ferrocenes.

^f Centers calculated for each of an AB pair.

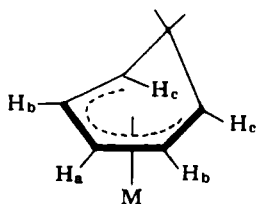
these molecules, the chain of atoms connecting the two rings is short enough to cause tilting of the normally parallel rings (XXV) (303, 46). Although it was first reported that the protons in such rings differed in chemical shift



(XXV)

by about 0.74 ppm, more recent reports (309) disagree with this. On the other hand, the later report contains data for other bridged ferrocenes in which a chemical shift difference for the ring protons is observed (leading to an A_2B_2 or an A_2X_2 set of two triplets, Table XVIII).

The $\pi-(C_5)M$ system is also found in olefin complexes (XXVI) containing the π -cyclohexadienyl (C_6H_7) radical. This series would be expected to give

 $\pi-(C_6H_7)M$

(XXVI)

a resonance pattern typical of an AB_2C_2 system, with additional resonances for the methylene group. The lines for H_a generally appear at lowest field, similar to the analogous proton resonances in some of the previously discussed complexes. The NMR spectral data reported for some of these complexes are listed in Table XVIII. The same problem concerning the assignment of methylene proton resonances is encountered here as for the analogous type of proton in the cyclopentadiene system [see $\pi-(C_4)M$, above]. The assignment of the resonances of the methylene protons is therefore omitted.

TABLE XIX
SUMMARY OF MAGNETIC RESONANCE DATA FOR COMPLEXES CONTAINING THE π -(C₆)M SYSTEM
AND FOR SOME OF THE FREE OLEFINS

Compound	τ [$\delta_{(\text{CH}_3)_4\text{Si}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
C ₆ H ₆ Ag ⁺ ^a						
H ₁	~ 4.6	—	—	—	$\delta_{\text{H}_2\text{O}} = 0$	328
H ₂	~ 5.0	—	—	—	40 Mc/sec	
H ₃	~ 5.2	—	—	—		
C ₆ H ₆ FeC ₆ H ₈	5.13	—	—	—	C ₆ H ₈ ; see Table XV	121
C ₆ H ₆ RuC ₆ H ₈	5.0	—	—	—	56.45 Mc/sec; CCl ₄ C ₆ H ₈ ; 181 See Table XV	
C ₆ H ₆ ReC ₆ H ₇	5.35	—	—	—	56.45 Mc/sec; C ₆ H ₈ C ₆ H ₇ ; see Table XVIII	181
C ₆ H ₆ Cr(CO) ₃ ·H ⁺						
C ₆ H ₆	—	—	—	—	56.45 Mc/sec	86
M—H	13.55	—	b	—	BF ₃ ·H ₂ O	
<i>Substituted Benzenes</i>						
(C ₆ H ₅ ·CH ₃)Cr(CO) ₃ ·H ⁺						
C ₆ H ₅	3.35	—	—	—	56.45 Mc/sec	86
CH ₃	7.14	—	—	—	BF ₃ ·H ₂ O soln	
M—H	13.98	—	b	—		
(C ₆ H ₅ ·(CH ₃) ₃)Cr(CO) ₃ ·H ⁺						
C ₆ H ₅	4.13	—	—	—	56.45 Mc/sec	86
CH ₃	7.78	—	—	—	BF ₃ ·H ₂ O soln	
M—H	14.27	—	b	—		

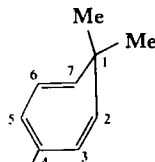
C_7H_8 cycloheptatriene					—	—	—	See Table XV			
$C_7H_8Cr(CO)_3$											
H_a					3.99	—	2×2	$J_{ab} = 4.8$ $J_{ab'} = 2.8$	CCl_4 56.4 Mc/sec $22^\circ \pm 1^\circ$	27	
H_b					5.17	—	c	—			
H_c					~ 6.6	—	c	—			
CH_2					$\left\{ \begin{array}{l} 7.1 \\ 8.23 \end{array} \right.$	—	AB pair 2	$J_{AB} = 12.6$			
$C_7H_8Mo(CO)_3$											
H_a					3.95	—	2×2	$J_{ab} = 4.8$ $J_{ab'} = 2.8$	CCl_4 56.45 Mc/sec $22^\circ \pm 1^\circ$	27	
H_b					5.11	—	5	$J_{ab}, J_{bc} \simeq 4$		206	
H_c					~ 6.5	—	$2 \times 3 ?$	—			
$\text{>}CH_2$					$\left\{ \begin{array}{l} \sim 6.9 \\ \sim 7.55 \end{array} \right.$	—	c 2	AB pair $J_{AB} = 12$			
$C_7H_8W(CO)_3$											
H_a					3.96	—	2×2	—	CCl_4 56.45 Mc/sec $22^\circ \pm 1^\circ$	27	
H_b					5.18	—	c	—			
H_c					$\left\{ \begin{array}{l} 6.1 \\ \text{to} \\ 7.2 \end{array} \right.$	—	c	—			
$\text{>}CH_2$											
<i>Substituted Cycloheptatrienes</i>											
1,1,4-Trimethylcycloheptatriene											
$C_7H_8 \cdot (CH_3)_3$											
					H_5	3.81	—	2	$J_{5,6} = 6.2$	56.4 Mc/sec	27
					H_6	4.12	—	2×2	$J_{6,7} = 9.0$		
					H_3	4.17	—	2	$J_{3,2} = 9.0$		
					H_2	$\left\{ \begin{array}{l} 5.07 \\ 5.04 \end{array} \right.$	—	2	} AB pair		
					H_7		—	2			
Me											
$CH_{3(4)}$					8.01	(3)	—	—			
$CH_{3(1)}$					9.03	—	—	—			

TABLE XIX—continued

Compound	τ [$\delta_{(\text{CH}_3)_{\text{Si}}} = 10$]	Relative Intensity	Multi- plicity	γ (cps)	Remarks	References
[C₇H₅(CH₃)₃]Mo(CO)₃						
H ₅	4.12	—	2	$\gamma_{5,6} = 7.2$	CCl ₄ 56.45 Mc/sec	27
H _{2,7}	6.52	—	2	$\gamma_{2,3}\gamma_{7,6} = 9.5$		
CH ₃₍₄₎	7.48	—	1	—		
CH ₃₍₁₎	8.60	—	1	—		
	9.70	—	1	—		
1,1,3,4-Tetramethylcycloheptatriene C₇H₄(CH₃)₄						
H ₅	3.84	—	2	$\gamma_{5,6} = 6.2$	CCl ₄ 56.45 Mc/sec	27
H ₆	4.22	—	2 × 2	$\gamma_{6,7} = 9.6$		
H ₇	5.03	—	2	—		
H ₂	5.16	—	~ 1	—		
CH ₃₍₄₎	8.03	(3)	1	—		
CH ₃₍₃₎	8.15	(3)	1	$\gamma_{\text{CH}_3-\text{H}_{(2)}} = 1.2$		
CH ₃₍₁₎	9.06	(6)	1	—		
[C₇H₄(CH₃)₄]Mo(CO)₃						
H ₅	4.02	—	2	$\gamma_{5,6} = 7.1$	CCl ₄ 56.45 Mc/sec	27
H ₆	5.31	—	2 × 2	$\gamma_{6,7} = 9.0$		
H ₇	6.28	—	2 × 3 ?	$\gamma_{7,6} = 8.6$		
H ₂	6.44	—	1	—		
CH ₃₍₄₎	7.49	—	1	—		
CH ₃₍₃₎	7.94	—	2	$\gamma_{\text{CH}_3-\text{H}_{(2)}} = 1.5$		
CH ₃₍₁₎	8.63	—	—	—		
	9.77	—	—	—		

$C_9H_{10}Mo(CO)_3^b$						
(C ₆)M	~ 4.5	(3)	—	—	$\delta_{HMDS} = 40 \text{ Mc/sec}$	206
C ₂ H ₄	{ ~ 7.1	(1)	—	—	CS ₂ soln	
	{ ~ 7.8	(1)	—	—		
$C_6H_6FeC_6H_8$						
C ₆ H ₆	5.13	6	—	—		120
CH of C ₆ H ₈	5.42	2	—	—		
	7.48	2	—	—		
CH ₂	8.6	4	—	—		
$C_6H_6RuC_6H_8$						
C ₆ H ₆	5.00	6	—	—		120
CH of C ₆ H ₈	5.08	2	—	—		
	6.73	2	—	—		
CH ₂	8.17	4	—	—		
$C_6H_6OsC_6H_8$						
C ₆ H ₆	5.08	6	—	—		120
CH of C ₆ H ₈	4.68	2	—	—		
	6.58	2	—	—		
CH ₂	8.08	4	—	—		

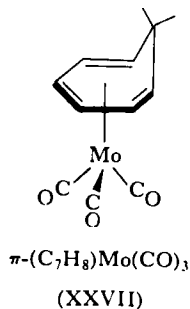
^a For H₁, $\delta = -0.65$; H₂, $\delta = 0.15$; H₃, $\delta = 0.00$ ppm.

^b For (C₆)M, $\delta = -5.5$; C₂H₄, $\delta = -2.9$ and -2.15 ppm.

It is likely that the $\pi-(C_5)M$ system also exists in certain protonated olefin complexes, such as $(C_7H_8 \cdot H^+)Fe(CO)_3$, or $(C_8H_8 \cdot H^+)Fe(CO)_3$ (Table XVIII). It would be of particular interest to know whether there is a three-membered ring system in the protonated cyclooctatetraene complex. The olefin resulting from neutralization of this cation with hydride ion, $(C_8H_{10})Fe(CO)_3$ is believed to contain the three-membered ring by virtue of a very high field resonance characteristic for methylene protons of a cyclopropyl ring [as discussed under $\pi-(C_4)M$, above]. In the protonated complex, this high-field line is absent, but of course, the entire proton resonance pattern is shifted somewhat to lower field on account of the positive charge in the complex. By analogy with known cyclopropyl substituted carbonium ions and other cyclopropane derivatives (cf. references cited in 379a) the NMR spectrum is just what would be expected for the bicyclic structure.

Complexes Containing the $\pi-(C_6)M$ System. In this category we have included the complexes of benzene and substituted benzenes, which generally show one resonance line in approximately the same region as the single line for cyclopentadienyl rings (Table XIX). The complex between benzene and silver ion has also been included in Table XIX. This does not necessarily imply that a $\pi-(C_6)M$ type of bond is present. The silver ion may well be involved with less than the full number of six carbon atoms of this ligand. However, the structure in solution is not known for this complex.

The $\pi-(C_6)M$ system is also present in the complexes of cycloheptatriene (C_7H_8) , when this olefin is bonded to transition metals requiring six π electrons, such as the metals of the chromium subgroup (27) (Table XIX). It should be noted that in its complexes with the *iron carbonyls*, this ligand is bonded as a $\pi-(C_4)M$ system. It was ascertained through chemical and spectroscopic evidence that the third olefinic bond was not participating in coordination to the metal (48) (Table XV).

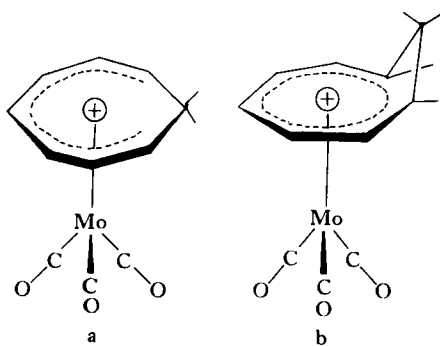


The structure for $(C_7H_8)Mo(CO)_3$ (XXVII) has been determined by X-ray study (102). This work showed that the methylene group is situated above the plane containing the rest of the olefin, on the side away from the metal. There were no unusual spectroscopic features (in particular no unusually low C—H stretching frequencies) associated with either of the methylene protons [see discussion of $(C_5H_5\phi)CoC_5H_5$, under $\pi-(C_4)M$, above].

The $\pi-(C_6)M$ system is believed to exist in the complex $C_9H_{10}Mo(CO)_3$ (207), listed in Table XIX, and possibly in the complexes of azulene [see discussion of $\pi-(C_4)M$ systems and Table XVI, above].

Complexes Containing the $\pi-(C_7)M$ System. The seven-carbon π -electron system is the largest presently believed to be engaged in π bonding as a unit from a single olefinic ligand to a metal atom. The first well-characterized complex containing such a system is the vanadium compound $C_7H_7VC_5H_5$ (206), for which the originally proposed structure, one with parallel coplanar rings, has been completely confirmed by an X-ray diffraction study (105). This complex is paramagnetic, so no NMR spectrum has been observed, but it may however be possible to determine some contact-interaction shifts, as have been reported for some paramagnetic metallocenes [see $\pi-(C_5)M$, above].

Magnetic resonance data are available for diamagnetic $C_7H_7CrC_5H_5$ (115). The spectrum consists of a singlet attributable to the C_5H_5 ring (see Table XVII) and a singlet for the C_7H_7 ring, at $\tau = 5.08$, C_6D_6 solution. King reports $\tau = 4.45$ (CS_2) and 4.59 (C_6H_6) for the C_7H_7 resonance (197, 198). The proton NMR spectrum for the seven-membered ring in $C_7H_7Mo(CO)_2(C_5H_5)$ is discussed in the section on $\pi-(C_4)M$ compounds,



(XXVIII)

because of the similarity of the problem of its single resonance line to that in the cyclooctatetraene complex of iron carbonyl.

The seven-membered ring system symmetrically bonded to a metal atom probably also exists in the cationic complex, $C_7H_7Mo(CO)_3^+$ (81). Chemical shifts for the series of salts $C_7H_7^+M(CO)_3BF_4^-$ in liquid SO_2 are: $M = Cr$, $\tau = 3.42$; $M = Mo$, $\tau = 3.82$; and $M = W$, $\tau = 3.83$; for $C_7H_7^+BF_4^-$ in liquid SO_2 , $\tau = 0.72$ (223a).

The complex $C_8H_8Mo(CO)_3$ (379a) can be protonated to examine the 6π -electron on the 7-carbon atom [$6\pi-(C_7)$] system in the cation (XXVIII). Especially interesting is the question whether (XXVIII) is cyclooctatrienyl (XXVIIIa) or monohomotropylum (XXVIIIb) in character. The NMR spectrum of this cation (379a) in comparison with those of free $C_8H_9^+$ (308a) and of $C_8H_9^+Fe(CO)_3$ (325, 87) shows it to be (XXVIIIb). The different electronic requirements of transition metal atoms in their complexes exert a corresponding control on the resulting structure and thus constitute a powerful tool in the study of various aspects of homoconjugation, homoaromaticity and nonclassical structures [cf. references cited in (379a)].

The spectrum of $C_7H_7V(CO)_3$ is worth particular mention. Fritz and Kreiter (132b) found a single sharp resonance at $-50^\circ C$, in agreement with the crystal structure which showed a ring centrosymmetrically bonded to the metal. However, at higher temperatures this resonance broadened into an unresolved multiplet which can only be interpreted in that less symmetry exists in the attachment of the ring to metal. This is indeed an unusual and unprecedented observation.

III

TIME-DEPENDENT PHENOMENA

A. Alkyl Derivatives

A characteristic property of some organometallic systems is the exchange of alkyl groups from one metal to another. This was first observed in the alkyl derivatives of aluminum, for instance, trimethylaluminum (260, 39, 154, 340). Although X-ray diffraction studies of the solid, and vapor density measurements and colligative properties in solution, indicate dimerization through methyl groups, thereby rendering the two groups different from the other four in Me_6Al_2 , only one resonance was observed at room temperature. At lower temperatures (-75°) two peaks appear, one at lower field (0.75 ppm) for the bridge methyl groups, and the other at higher field

(0.38 ppm) for the terminal methyl groups, shifted from the single resonance which appears at the weighted average position between these two at room temperature. For alkylaluminum halides, no significant shift in resonance was found between the room-temperature and low-temperature spectra, from which it was deduced that the halogens are chiefly responsible for the bridging (340, 154). It was found that for mixtures of alkoxyaluminum dialkyls with trialkylaluminum derivatives, even at room temperature it was possible to observe a discernible resonance for the methyl groups bonded to aluminum in the former which occurred at higher field than for those in the latter (175). Apparently the alkoxy group rather than two methyl groups in the alkoxyaluminum dialkyl is favored in the participation of metal bridging, with the exception of *tert*-BuOAlR₂. In the latter some temperature dependence was observed for the alkyl resonance, denoting its participation in bridging in favor of the alkoxy group, which in this case is a highly branched one. The interplay between steric and electronic factors in determining the most favorable group for bridging is quite interesting.

Exchange of alkyl groups may take place between different metals or the same metal in two different oxidation states in which there are two characteristic resonances. A single resonance at the weighted average chemical shift position will be observed. Such exchange was noted in solutions of trimethylaluminum and dimethylzinc and in solutions of dimethylzinc and dimethylcadmium (245). The exchange may be slowed by dilution to the point where a characteristic resonance is observed for each of the two components. From temperature or concentration dependence of the collapse of the two characteristic resonances, or the analysis of the line shape, it is possible to estimate an average lifetime of each species before exchange and also obtain the activation energy for the exchange process (9, 245, 290, pp. 219 ff.).

In a pure metal alkyl if isotopes of the metal of appropriate magnetic activity are present, the collapse of metal-proton spin-spin coupling satellites will be a clue to any exchange occurring. In alkylmercury derivatives, for instance, at room temperature the proton resonances are accompanied by metal spin-spin coupling satellites (91). This of course simply places a minimum for the lifetime of the species before exchange, and other experiments such as isotope labeling must be used to check for exchange processes over a longer period of time.

No exchange is noted between R₂Hg and RHgX (X = Cl and Br) (160, 295a). At room temperature each of these species exhibits its own character-

istic resonance. At higher temperatures, however, it is possible to see these separate resonances collapse into one (and at the same time observe the disappearance of the metal-proton spin-spin coupling satellites) (295a). It is interesting to note that the salts RHgI show either no or greatly broadened metal-proton spin-spin coupling satellites even at room temperature, indicating a greater tendency towards alkyl exchange compared with the bromides or the chlorides (160, 295a).

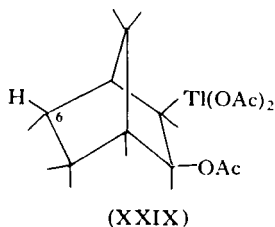
Magnetic resonance has been applied to the study of the Grignard reagents. In 3,3-dimethylbutylmagnesium chloride, $(\text{CH}_3)_2\text{CCH}_2\text{CH}_2\text{MgCl}$, a low-temperature form (-53°C) shows methylene hydrogens which are magnetically unequivalent, giving rise to an $\text{AA}'\text{XX}'$ pattern. At higher temperature (32°C), these become an A_2X_2 system. The corresponding dialkylmagnesium reagent showed the same behavior but at a higher temperature range ($\text{AA}'\text{XX}'$ at 28° , and A_2X_2 at 110°C) (371). These observations can be explained by other means than invoking an alkyl-metal exchange reaction, however.

The question of the constitution of the Grignard reagent, certainly in solution, is not yet settled (18). The NMR favors the formulation $\text{R}_2\text{Mg}\cdot\text{X}_2\text{Mg}$ because chemical shifts in R_2Mg are very close to what they are observed in " RMgX " (107, 271, 308). Comparison with other derivatives containing the metal in two different oxidation states such as R_2Hg and RHgX (see above) would lead us to expect that the chemical shifts for the corresponding two derivatives of magnesium would also be different, but they are not. Even in the presence of rapid exchange between R_2M and RMX a weighted average chemical shift position would be seen which would be different than for pure R_2M . Therefore the NMR data favor the species $\text{R}_2\text{Mg}\cdot\text{X}_2\text{Mg}$ to explain the chemical shifts. Yet a direct structure determination of phenylmagnesium bromide dietherate shows magnesium bonded to two ether molecules, one halogen and one phenyl group (tetrahedrally distributed about the metal) (350). These authors offer cogent arguments about retaining this configuration even in solution. Finally, it should be noted that some earlier exchange work favoring the formulation $\text{R}_2\text{Mg}\cdot\text{X}_2\text{Mg}$ has been shown under certain circumstances not to be reproducible.⁷ And so, even after over 60 years of study, this important reagent of chemistry remains an enigma.

Rapid intermolecular exchange of groups is also occurring in organo-thallium compounds at room temperature, since metal-proton spin-spin

⁷ See the chapter by Dessy in Volume 4 of *Advances in Organometallic Chemistry*.

coupling satellites are not observed (220, 221, 222). This exchange can be slowed down by reducing the temperature, or by introducing electron pair donor molecules which coordinate with the metal and thus greatly decrease its tendency to form polymers in which alkyl groups are the bridging ligands (220). On the other hand in alkylthallium salts such as R_2Tl^+ and RTl^{2+} the metal-proton spin-spin coupling satellites are observed even at room temperature (12a, 159, 222). In this respect, it is interesting to note the

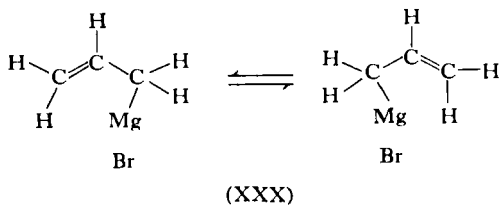


large coupling constant observed for the long-range interaction $Tl^{205}-H_6$ (817 cps) in compound (XXIX) (12a).

B. Alkenyl Derivatives and Olefin π Complexes

In this class of compound a phenomenon in addition to metal-ligand interchange is observed, the exchange of metal-to-carbon bond from one site to another in the same ligand, *i.e.* valence tautomerism after Pettit (223a). This usually causes the averaging of chemical shifts for protons in different magnetic environments in the frozen molecule, but it will preserve metal-proton spin-spin coupling satellites although the observed splittings will be the average of the extreme values in the frozen molecule.

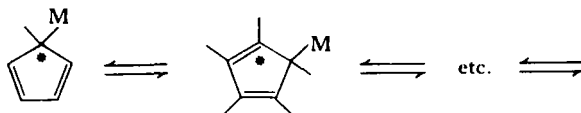
In allylmagnesium bromide there is some rapid equilibration in solution which causes the two terminal CH_2 groups to appear equivalent, giving the resonance for an AX_4 group (268). The two isomers (XXX) are interconverted faster than 1000 times per second even down to $-80^\circ C$. This is distinctly different than the π -allyl group bonded to transition metals which



appears as an AB_2C_2 spectrum. The AX_4 pattern is also observed for allyllithium (179).

Butenyl- and dimethylallylmagnesium bromides (271, 372) exist predominantly as the primary isomers, i.e., $CH_3CH=CHCH_2MgBr$ and $(CH_3)_2C=CHCH_2MgBr$, respectively. For the latter, resonance of the methyl groups is split into a doublet at lower temperature ($-26^\circ C$), indicating that at room temperature some rapid motion is causing equilibration of the two methyl groups. Presumably this is the same process as depicted for allylmagnesium bromide (XXX) but the chemical shifts indicate that equilibrium must lie far on the side of the primary isomer.

For the sigma-bonded cyclopentadienyl group, a somewhat similar equilibration process as in allylmagnesium bromide is occurring causing the resonance to appear as a single line at an averaged chemical shift position.



This has been observed for sigma-bonded C_5H_5 derivatives of heavy metals and some transition metals, i.e. $(C_5H_5)_2Hg$, $\sigma-C_5H_5Fe(CO)_2$ ($\pi-C_5H_5$) (283) and most recently for derivatives of tin and lead (133b, 132c). The sigma-bonded C_5H_5 derivatives of some of the lighter elements, like Si, show the A_2B_2X pattern expected for a longer lived $M-C$ bond. However, in the pyrrole Grignard reagent (299) rapid equilibration between several $Mg-C$ sites is occurring just as in the cyclopentadienyl derivative of that metal.

In closing, we should add some brief remarks about coordination compounds of olefins. Cramer (75) explains the broad resonance of coordinated ethylene in $(\pi-C_5H_5)Rh(CH_2=CH_2)_2$ (193) [Section II, 13, 3], as due to rotation of that ligand around the coordinate bond axis. This would be similar to the interpretation of Mulay, Rochow, and Fischer (257a) of rotation of rings about the coordinate bond axis in ferrocene and dibenzenechromium in their study of linewidths in broad line NMR.

Inability to observe metal-proton coupling satellites in certain silver complexes (mentioned in the discussion in various places above) could be interpreted to denote rapid exchange of olefin between different metal atoms. In view of the small coupling constants for metals in the second transition series however [cf. small coupling constants for rhodium, $\pi-(C_5)M$ discussion above], it may be that the satellites simply are not resolvable from the

main resonance. Further work is needed to clarify this point. In some olefin complexes of platinum in which the resonances were observed to be broad (see above) the absence of metal-proton spin-spin coupling satellites (which should be more widely separated from the main resonance in complexes of a metal from the third transition series) is compelling evidence that olefin-metal exchange is occurring. In such cases, it is possible that a slight amount of free olefin (if any is present in excess or through small dissociation of complex) is exchanging with complexed olefin, by analogy with the discovery (75) that in some complexes of rhodium with ethylene, free ligand will exchange with coordinated ligand.

Finally, an intramolecular exchange similar to that noted for alkenyl derivatives has been noted for some olefin complexes. In each of these cases, the olefin offers more centers of unsaturation than the metal is believed capable of accepting (in terms of the Effective Atomic Number Rule) in any one frozen structure. This should lead to the appearance of different kinds of protons in the ligand. However, single resonances are usually observed. In some cases, structure studies show that in the solid state the metal is indeed associated with only some of the olefinic sites, for instance as in $C_8H_8Fe(CO)_3$ (see above). The most reasonable possibility is that in solution the metal is rapidly exchanging internally with all the olefinic sites; some prominent examples may be cited, such as $(C_8H_8)Fe(CO)_3$ (228), $C_7H_7Mo(CO)_2(\pi-C_5H_5)$ (197), benzene- Ag^+ (136), and $C_7H_7Fe(CO)_3^+$ (223a)⁸. In most cases, these time-dependent phenomena have not become frozen even at $-78^\circ C$. These will require further work in order to provide concrete evidence for the above mentioned interpretation. In contrast with this behavior is the resonance of $C_7H_7V(CO)_3$ [see $\pi-(C_7)M$, above] which shows a sharp resonance at low temperatures and a multiplet at higher temperatures (132b).

⁸ A large number of additional examples of this phenomenon principally for complexes of iron carbonyls has been reported by Pettit and co-workers [cf. (187a) and references cited therein]. Such internal exchange is termed by these authors as *valence tautomerism*.

The complex $C_8H_8Mo(CO)_3$ also displays this phenomenon (379a); NMR of this in toluene solution shows a sharp singlet at $70^\circ C$, which becomes broadened (half-width 25 cps) at room temperature and freezes to a complex pattern at $-30^\circ C$. This is therefore the first known complex of cyclooctatetraene whose proton magnetic resonance shows observable change from rapid to arrested valency tautomerism.

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APPENDIX FORMULA INDEX

Formula	Table	Formula	Table
CH ₃ BF ₃	I	CH ₃ HgI	I
CBF ₆	IV	CH ₃ HgNO ₃	I
CH ₃ BrHg	I	CH ₃ IMg	I
CH ₃ ClHg	I	CH ₃ Li	I
CH ₃ ClHgO ₄	I	CH ₄ Cl ₂ Si	I
CH ₃ Cl ₃ Si	I	CH ₄ HgO	I
CH ₃ Cl ₃ Sn	I	CH ₆ Sn	I

Formula	Table	Formula	Table
$C_2BCl_2F_3$	VIII	C_3H_5NO	XII
C_2BF_5	VIII	$C_3H_6ClF_3Sn$	I, IV
$C_2H_3BCl_2$	V	$C_3H_6HgO_2$	I
$C_2H_3BF_2$	V	C_3H_6NSTl	I
$C_2H_3BF_3$	V	C_3H_6NTl	I
C_2H_3BrMg	V	$C_3H_7BF_2$	III
C_2H_3ClMg	V	C_3H_9Al	I
$C_2H_3Cl_2O_8Tl$	V	C_3H_9As	I
C_2H_3HgN	I	C_3H_9B	I
C_2H_3HgNS	I	C_3H_9Bi	I
C_2H_3Li	V	C_3H_9BrSn	I
$C_2H_4Cl_3KPt$	X	C_3H_9ClSi	I
$C_2H_5BCl_2$	II	C_3H_9ClSn	I
$C_2H_5BF_2$	II	C_3H_9GeLiO	I
C_2H_5BrHg	II	$C_3H_9GeLiSe$	I
C_2H_5BrMg	II	$C_3H_9Hg_3O_4P$	I
$C_2H_5Cl_3Si$	II	C_3H_9In	I
C_2H_5ClHg	II	C_3H_9LiSn	I
$C_2H_5ClHgO_4$	II	C_3H_9N	I
C_2H_5F	II	$C_3H_9NO_3Pb$	I
C_2H_5HgI	II	C_3H_9P	I
$C_2H_5HgNO_3$	II	C_3H_9S	I
C_2H_5Li	II	C_3H_9Tl	I
$C_2H_6Al_2Cl_4$	I	$C_3H_{10}Si$	I
C_2H_6Cd	I	$C_3H_{10}Sn$	I
$C_2H_6ClO_4Tl$	I	$C_3H_{10}Pb$	I
$C_2H_6Cl_2Si$	I		
$C_2H_6Cl_2Sn$	I	C_4F_6Hg	VIII
C_2H_6FTl	I	$C_4H_2O_3$	X
C_2H_6Hg	I	C_4H_3HgO	VI
$C_2H_6Hg_2O_4S$	I	C_4H_6	XV
$C_2H_6HgO_2$	III	C_4H_6BCl	V
$C_2H_6Hg_2S$	I	$C_4H_6ClO_4Tl$	V
C_2H_6ITl	I	$C_4H_6F_3O_2Tl$	I
C_2H_6Mg	I	C_4H_6Hg	V
$C_2H_6MnO_4Tl$	I	$C_4H_6Hg_2O_4$	I
C_2H_6Se	I	$C_4H_6O_2$	XII
C_2H_6Te	I	C_4H_7BrMg	VI
C_2H_6Zn	I	C_4H_8	X
C_2H_7ClSi	I	$C_4H_8AgNO_3$	X
C_2H_7OTl	I	$C_4H_8Cl_3KPt$	X
C_2H_8Sn	I	$C_4H_8Cl_4Pt_2$	X
		$C_4H_8F_4Sn$	I
C_3H_4Hg	I	$C_4H_8F_4Sn$	IV
C_3H_4O	XII	C_4H_9B	I, V
$C_3H_4O_2$	XII	C_4H_9BrMg	III
C_3H_5HgN	II	$C_4H_9F_3Sn$	I
C_3H_5Li	II, VI	$C_4H_9F_3Sn$	IV

Formula	Table	Formula	Table
C_4H_9Li	III	C_6F_8	XV
C_4H_9Tl	I	$C_6F_{14}IP$	IV
$C_4H_{10}AlCl$	II	$C_6H_3MnO_5$	I
$C_4H_{10}Cd$	II	$C_6H_4ClCoO_3$	XIV
$C_4H_{10}ClO_4Tl$	II	C_6H_4Hg	III
$C_4H_{10}ClSi$	II	$C_6H_4O_2$	X
$C_4H_{10}Cl_2Sn$	II	$C_6H_5BCl_2$	VII
$C_4H_{10}Hg$	II	$C_6H_5Cl_2O_8Tl$	VII
$C_4H_{10}Mg$	II	$C_6H_5Cl_3Si$	VII
$C_4H_{10}NO_3Tl$	II	$C_6H_5CoO_3$	XIII
$C_4H_{10}Se$	II	C_6H_5IOPt	XVII
$C_4H_{10}Te$	II	$C_6H_6Ag^+$	XIX
$C_4H_{10}Zn$	II	$C_6H_6F_6Ge$	VIII
$C_4H_{11}Tl$	I, II	$C_6H_6F_6Sn$	VIII
$C_4H_{12}Al_2Cl_3$	I	$C_6H_6F_{10}Sn$	IV
$C_4H_{12}CrO_4Tl_2$	I	$C_6H_7BO_2$	VII
$C_4H_{12}Ge$	I	C_6H_7Na	VI
$C_4H_{12}O_4STl_2$	I	C_6H_8	XV, XVIII
$C_4H_{12}Pb$	I	$C_6H_8CrN_2O_2$	I, XVII
$C_4H_{12}Si$	I	$C_6H_8F_8Sn$	I, IV
$C_4H_{12}Sn$	I	$C_6H_8O_4$	X
$C_4H_{14}Al_2$	I	C_6H_9As	V
$C_4H_{14}AlN$	I	C_6H_9B	V
		C_6H_9ClSn	V
$C_5F_3FeIO_4$	IV	C_6H_9Ga	V
$C_5H_4O_3$	X	C_6H_9Sb	V
$C_5H_5ClMoO_2$	XVII	C_6H_9Si	VI
$C_5H_5CrINO_2$	XVII	C_6H_{10}	X, XV
C_5H_5NNiO	XVII	$C_6H_{10}Ag^+$	X
C_5H_6	XV	$C_6H_{10}Br_2Ni_2$	XIII
$C_5H_6AgClO_4$	XV	$C_6H_{10}Br_2Pd_2$	XIII
C_5H_6OPd	XIII	$C_6H_{10}Cl_2Pd_2$	XIII
C_5H_9B	I, V	$C_6H_{10}Hg$	VI
C_5H_9BrMg	VI	$C_6H_{10}I_2Pd_2$	XIII
C_5H_9Tl	I	$C_6H_{12}Si$	I, V
$C_5H_{10}HgO_2$	III	$C_6H_{14}Cd$	III
$C_5H_{10}NSTl$	II	$C_6H_{14}Ge$	I, VI
$C_5H_{11}O_3Tl$	I	$C_6H_{14}Hg$	III
$C_5H_{12}O_3Tl_2$	I	$C_6H_{14}Sn$	I, VI
$C_5H_{12}Si$	I, V	$C_6H_{15}Al$	II
$C_5H_{16}AlN$	I, II	$C_6H_{15}B$	II
$C_5H_{13}Tl$	I, II	$C_6H_{15}Ga$	II
		$C_6H_{15}P$	II
C_6AsF_9	VIII	$C_6H_{15}FSi$	II
C_6BF_9	VIII	$C_6H_{15}Tl$	II
$C_6ClF_{14}P$	IV	$C_6H_{16}O_2Sn$	II
$C_6F_3MnO_5$	IV	$C_6H_{17}AlCl_2N_2$	II
$C_6F_5FeIO_4$	IV	$C_6H_{18}Al_2$	I

Formula	Table	Formula	Table
$C_6H_{18}Al_2O_2$	I	$C_8HF_4MnO_6$	IV
$C_6H_{18}BN$	I	$C_8H_2F_8FeO_4$	IV
$C_6H_{18}Ge_2$	I	$C_8H_2FeO_7$	X
$C_6H_{18}GeOSi$	I	$C_8H_4FeO_4$	XV
$C_6H_{18}Ge_2O$	I	$C_8H_5MnO_3$	XVII
$C_6H_{18}Ge_2Se$	I	$C_8H_6CrO_3$	XVII
$C_6H_{18}OPbSi$	I	$C_8H_6FeO_6$	XII
$C_6H_{18}OSi_2$	I	$C_8H_6MoO_3$	XVII
$C_6H_{18}OSiSn$	I	$C_8H_6O_3W$	XVII
$C_6H_{18}OSn_2$	I	$C_8H_7O_3W^+$	XVII
$C_6H_{18}O_4PTl_3$	I	C_8H_8	X, XV
$C_6H_{18}SeSn_2$	I	$C_8H_8AgNO_3$	X
$C_6H_{18}Si_2$	I	$C_8H_8Cl_2Pt$	X
$C_6H_{18}Sn_2$	I	$C_8H_8FeO_2$	I, XVII
		$C_8H_8FeO_3$	XV
$C_7F_7FeIO_4$	IV	$C_8H_8I_2Pt$	X
$C_7F_5MnO_5$	IV	$C_8H_8O_4Re^+$	X
$C_7F_5O_5Re$	IV	$C_8H_8BF_4FeO_3$	XIV
$C_7HClF_3MnO_5$	IV	$C_8H_9CoO_3$	XIV
$C_7HCl_2F_2MnO_5$	IV	$C_8H_{10}BrCo$	XIII, XVII
$C_7HF_4MnO_5$	IV	$C_8H_{10}CoI$	XIII, XVII
$C_7H_4FeO_3$	XV	$C_8H_{10}F_6Si$	VIII
$C_7H_4FeO_5$	XII	$C_8H_{10}Ni$	XIII, XVII
$C_7H_4FeO_6$	XII	$C_8H_{10}Pd$	XIII, XVII
$C_7H_5CoO_2$	XVII	$C_8H_{10}Pt$	XIII, XVII
$C_7H_5F_6MnNO_3P$	XVII	C_8H_{12}	X
$C_7H_5FeNO_5$	XII	$C_8H_{12}Cl_4Pd_2$	XIV
$C_7H_5IrO_2$	XVII	$C_8H_{12}O_4$	X
$C_7H_5MnO_4$	XIII	$C_8H_{12}Pb$	V
$C_7H_5MnO_5$	II	$C_8H_{12}Si$	I, V, VII
$C_7H_6FeO_3$	XV	$C_8H_{12}Sn$	V
$C_7H_7ClFeO_3$	XIV	$C_8H_{13}ClHgO$	III
$C_7H_7CoO_3$	XIV	$C_8H_{14}Cl_2Pd_2$	XIV
$C_7H_7FeIO_3$	XIV	$C_8H_{14}O_2Pd$	XIV
C_7H_8	X, XV, XIX	$C_8H_{15}As$	V
C_7H_{10}	XV	$C_8H_{15}F_3O_3Si$	VIII
$C_7H_{15}O_3Tl$	II	$C_8H_{15}F_3Ge$	VIII
$C_7H_{20}AlN$	II	$C_8H_{15}F_3Si$	VIII
$C_7H_{20}Sn_2$	I	$C_8H_{15}F_3Sn$	VIII
$C_7H_{21}AlN_2$	I	$C_8H_{15}F_5Sn$	IV
		$C_8H_{20}Ge$	II
$C_8F_5MnO_5$	IX	$C_8H_{20}Si$	II
$C_8F_5MnO_6$	IV	$C_8H_{20}Sn$	II
$C_8F_5O_6Re$	IV	$C_8H_{20}Pb$	II
$C_8F_7MnO_5$	IV	$C_8H_{22}AlClN_2$	II
$C_8F_7O_5Re$	IV	$C_8H_{22}Al_2O_2$	I
$C_8F_{10}FeO_4$	IV	$C_8H_{23}AlN_2$	I
$C_8F_{12}Ge$	VIII	$C_8H_{24}Al_2Cl_2N_4$	II

Formula	Table	Formula	Table
$C_8H_{24}GeO_2Si_2$	I	$C_{10}H_8CrO_3$	XIX
$C_8H_{24}O_2Si_2Sn$	I	$C_{10}H_8DFeO_3^+$	XV, XVIII
$C_8H_{24}Sn_3$	I	$C_{10}H_8FeI_2$	XVIII
		$C_{10}H_8FeO_2$	XVII
$C_9F_7O_6Re$	IV	$C_{10}H_8FeO_3$	X, XV
$C_9F_9FeO_3$	XIV, XV	$C_{10}H_8FeO_8$	X
$C_9HF_6MnO_5$	IX	$C_{10}H_8Fe_2O_6S$	V, XII
$C_9H_4FeO_7$	X	$C_{10}H_8MoO_3$	XIX
$C_9H_6Fe_2O_6S$	V, XII	$C_{10}H_8O_3W$	XIX
$C_9H_6FeO_8$	X	$C_{10}H_9Cl_6FeO_2Sb$	XVII
$C_9H_6DMnO_3$	XVIII	$C_{10}H_9ClFeHg$	XVII, XVIII
$C_9H_7BF_4FeO_3$	XVIII	$C_{10}H_9CrO_3$	XIX
$C_9H_7CrO_3^+$	XIX	$C_{10}H_9FeI$	XVII, XVIII
$C_9H_7MnO_3$	XVIII	$C_{10}H_9FeO_3$	XV
$C_9H_8FeO_3$	III, XV, XVII	$C_{10}H_9FeO_3^+$	XVIII
$C_9H_8MoO_3$	I, XVII	$C_{10}H_9MnO_3$	XVIII
C_9H_8O	XII	$C_{10}H_{10}Co$	XVII
$C_9H_8O_2$	XII	$C_{10}H_{10}Cr$	XVII
$C_9H_8O_3W$	I, XVII	$C_{10}H_{10}CrNO_2$	XVII
$C_9H_9FeIO_2$	XVIII	$C_{10}H_{10}Cr_2N_4O_4$	XVII
C_9H_9FeN	XVII, XVIII	$C_{10}H_{10}CrNO$	VI
C_9H_{10}	XI	$C_{10}H_{10}DBF_4FeO_2$	VI, XII
$C_9H_{10}FeO$	XIII, XVII	$C_{10}H_{10}DClFeO_6$	XII
$C_9H_{10}FeO_2$	II, XVII	$C_{10}H_{10}DRe$	XVII
$C_9H_{11}BrMg$	III	$C_{10}H_{10}DClFeO_6$	XVII
$C_9H_{11}CoO_3$	XIV	$C_{10}H_{10}DCo$	XV, XVII
$C_9H_{12}CoIO$	XVII	$C_{10}H_{10}DFeO_2^+$	XII
$C_9H_{12}GeO_2$	I	$C_{10}H_{10}D_2ClRe$	XVII
$C_9H_{13}Rh$	X, XVII	$C_{10}H_{10}Fe$	XVII
$C_9H_{15}CrP$	VI	$C_{10}H_{10}FeO_2$	VI, XVII
$C_9H_{15}Ga$	VI	$C_{10}H_{10}FeO_3$	XV
$C_9H_{20}O_3Tl_2$	II	$C_{10}H_{10}FeO_3$	XVII
$C_9H_{24}AlN$	I	$C_{10}H_{10}FeO_4$	XV
$C_9H_{24}GeOSi$	I	$C_{10}H_{10}Hg$	III, VI
$C_9H_{24}OPbSi$	I	$C_{10}H_{10}Mn$	XVII
$C_9H_{27}NSi_2Sn$	I	$C_{10}H_{10}MoO_2$	XIII
		$C_{10}H_{10}MoO_3$	XVII
$C_{10}HF_8MoO_6$	IV	$C_{10}H_{10}Ni$	XVII
$C_{10}H_4FeO_6$	X	$C_{10}H_{10}O_3Re$	XVII
$C_{10}H_4Fe_2O_6$	XV	$C_{10}H_{10}OS$	XVII
$C_{10}H_5CoF_8O$	XVII	$C_{10}H_{10}O_2W$	XIII, XVII
$C_{10}H_5F_5FeO_2$	IX	$C_{10}H_{10}O_3W$	XVII
$C_{10}H_6D_2$	XVI	$C_{10}H_{10}Pb$	III, VI
$C_{10}H_6F_4MoO_3$	IV	$C_{10}H_{10}Ru$	XVII
$C_{10}H_6F_4O_3W$	IV, XVII	$C_{10}H_{10}Sn$	III, VI
$C_{10}H_6FeO_4$	XV	$C_{10}H_{10}V$	XVII
$C_{10}H_6Fe_2O_6S$	V, XII	$C_{10}H_{11}ClFeO_6$	XII, XVII
$C_{10}H_8$	XVI	$C_{10}H_{11}ClFeO_6$	XII

Formula	Table	Formula	Table
$C_{10}H_{11}Co$	XV, XVII	$C_{11}H_{10}Cl_3Co$	XV, XVII
$C_{10}H_{11}DFeO_2$	XVII	$C_{11}H_{10}CoF_3$	XV
$C_{10}H_{11}Fe^+$	XVII	$C_{11}H_{10}DFe_6MoO_3P$	XII, XVII
$C_{10}H_{11}FeNO_3$	III, XVII	$C_{11}H_{10}FeO_3$	XV
$C_{10}H_{11}FeO_2^+$	XII	$C_{11}H_{10}Fe_2O_6S$	V, XII
$C_{10}H_{11}Re$	XVII	$C_{11}H_{10}MoO_3$	VI, X, XVII
$C_{10}H_{11}Rh$	XV, XVII	$C_{11}H_{10}MoO_4$	XVII
$C_{10}H_{11}Ru^+$	XVII	$C_{11}H_{10}O_3W$	VI, XVII
$C_{10}F_{14}FeO_4$	IV	$C_{11}H_{10}O_4W$	XVII
$C_{10}H_{12}ClRe$	XVII	$C_{11}H_{11}DFe$	XV, XVII, XVIII
$C_{10}H_{12}FeO_2$	XVII	$C_{11}H_{11}Cl_2Co$	XV, XVII
$C_{10}H_{12}Mo$	XVII	$C_{11}H_{11}CrNO_3$	XVIII
$C_{10}H_{12}Ni$	XVII, XIV	$C_{11}H_{11}MoNO_3$	XVIII
$C_{10}H_{12}W$	XVII	$C_{11}H_{11}F_6MoO_3P$	XII, XVII
$C_{10}H_{13}Mo^+$	XVII	$C_{11}H_{11}F_6O_3PW$	XII, XVII
$C_{10}H_{13}Ta$	XVII	$C_{11}H_{12}DCiFeO_6$	XVII, XII
$C_{10}H_{13}W^+$	XVII	$C_{11}H_{12}DFeO_2^+$	XII
$C_{10}H_{14}$	XIX	$C_{11}H_{12}Fe$	XV, XVII, XVIII
$C_{10}H_{15}BO_2$	VII	$C_{11}H_{12}FeO_2$	VI, XVII
$C_{10}H_{18}Cl_2O_2Pd_2$	XIV	$C_{11}H_{12}MoO_3$	XVII
$C_{10}H_{18}Br_2O_2Pd_2$	XIV	$C_{11}H_{12}O_3W$	XVII
$C_{10}H_{18}F_3Sn$	VIII	$C_{11}H_{13}ClFeO_6$	XII, XVII
$C_{10}H_{18}O_2Pd$	XIV	$C_{11}H_{13}ClTi$	XVII
$C_{10}H_{18}Pt$	I	$C_{11}H_{13}Co$	XV, XVII
$C_{10}H_{18}AlO$	V	$C_{11}H_{13}FeO_2^+$	XII
$C_{10}H_{21}As$	V	$C_{11}H_{14}Pd$	XIV, XVII
$C_{10}H_{20}F_2OSi$	IX	$C_{11}H_{16}$	XIX
$C_{10}H_{21}ClSn$	V	$C_{11}H_{16}OPd$	XIV, XVII
$C_{10}H_{25}AlO$	II	$C_{11}H_{20}F_2Si$	IX
$C_{10}H_{25}GaO$	II	$C_{11}H_{20}O_2Pd$	XIV
$C_{10}H_{27}AlN_2$	II	$C_{11}H_{22}F_2SSi$	IX
$C_{10}H_{28}Al_2O_2Si_2$	II		
$C_{10}H_{30}Al_2O_2Si_2$	I	$C_{12}H_5F_6FeO_4$	XVII
$C_{10}H_{30}GeO_3Si_3$	I	$C_{12}H_5DF_6FeMnO_7P$	XVII
$C_{10}H_{30}O_3Si_3Sn$	I	$C_{12}H_6FeMnO_7$	XVII
		$C_{12}H_{10}ClF_3Ni$	XIV, XVII
$C_{11}F_5MnO_5$	VII	$C_{12}H_{10}Cl_2Si$	VII
$C_{11}H_5F_6MnO_2$	IX, XVII	$C_{12}H_{10}Cl_2Sn$	VII
$C_{11}H_6FeO_3S$	XII	$C_{12}H_{10}ClO_4Ti$	VII
$C_{11}H_8CrO_4$	X	$C_{12}H_{10}Co_2F_4$	XVII
$C_{11}H_8DFeO_3^+$	XVIII	$C_{12}H_{10}CrO_3$	XI
$C_{11}H_8DFeO_3$	XVI	$C_{12}H_{10}F_4Ni$	XIV, XVII
$C_{11}H_8FeO_3$	XV	$C_{12}H_{10}FeO_2$	VI, XVII
$C_{11}H_8FeO_4$	XV	$C_{12}H_{10}F_6FeO_2P$	XVII
$C_{11}H_8MoO_4$	X	$C_{12}H_{10}Mn_2N_2O_4$	XVII
$C_{11}H_9FeO_3$	XV	$C_{12}H_{10}MoO_3$	XI, XIX
$C_{11}H_9FeO_3^+$	XVIII	$C_{12}H_{10}O_2Pt_2$	XVII
$C_{11}H_{10}$	XVI	$C_{12}H_{10}O_3W$	XI

Formula	Table	Formula	Table
$C_{12}H_{11}FeO_2$	XVIII	$C_{13}H_6Mn_2O_{10}$	III
$C_{12}H_{11}O_2Re$	X, XVII	$C_{13}H_8FeO_5$	XII
$C_{12}H_{11}O_2Ru^+$	XVII	$C_{13}H_8FeO_6$	XII
$C_{12}H_{12}Cr$	XVII	$C_{13}H_{10}FeO_3$	XV
$C_{12}H_{12}CrO_2$	XIV, XVII	$C_{13}H_{12}FeO$	XVIII
$C_{12}H_{12}FeO$	XVII, XVIII	$C_{13}H_{13}Co$	X, XVII
$C_{12}H_{12}FeO_2$	XVII, XVIII	$C_{13}H_{13}Rh$	X
$C_{12}H_{12}FeO_3$	X	$C_{13}H_{14}$	XVI
$C_{12}H_{12}MnO_3$	XVIII	$C_{13}H_{14}Co$	XVII
$C_{12}H_{12}MoO_4$	X	$C_{13}H_{14}F_6MnP$	XVII
$C_{12}H_{12}OOs$	XVII	$C_{13}H_{14}Fe$	XVIII
$C_{12}H_{12}ORu$	XVII	$C_{13}H_{14}MoO_3$	XIX
$C_{12}H_{13}CrO_3^+$	XIX	$C_{13}H_{14}Si$	I, VII
$C_{12}H_{13}O_2Re$	X, XVII	$C_{13}H_{15}Co$	XV, XVII
$C_{12}H_{13}Re$	XVIII, XIX	$C_{13}H_{16}Cl_2N_2Pd$	III
$C_{12}H_{14}Fe$	XV, XVIII, XIX	$C_{13}H_{16}CrNO_3$	XVIII
$C_{12}H_{14}FeO_3$	XV	$C_{13}H_{16}MnNO_3$	XVIII
$C_{12}H_{14}Os$	XIX	$C_{13}H_{17}Co$	X
$C_{12}H_{14}Ru$	XV, XVIII, XIX	$C_{13}H_{17}Pd$	XIV
$C_{12}H_{14}Si$	V	$C_{13}H_{18}Pd$	XVII
$C_{12}H_{15}FeNO_3$	III, XVII	$C_{13}H_{20}OPd$	XIV, XVII
$C_{12}H_{16}Cl_2N_2Pt$	I	$C_{14}H_8Fe_2O_6$	XV
$C_{12}H_{16}Co_2S_2$	XVII	$C_{14}H_8Mn_2O_{10}$	III
$C_{12}H_{16}Ni$	XIV, XVIII	$C_{14}H_{10}Fe_2O_6$	XV
$C_{12}H_{16}Ti$	I, XVII	$C_{14}H_{10}O_4Os_2$	XVII
$C_{12}H_{18}Cl_2O_2Pd_2$	XIV	$C_{14}H_{11}Fe_2O_4^+$	XVII
$C_{12}H_{18}Cl_2Pd_2$	XIV	$C_{14}H_{12}Fe$	XVII, XVIII
$C_{12}H_{18}FeO_2$	XVIII	$C_{14}H_{12}MoO_2$	XVII
$C_{12}H_{18}Ge_2$	V	$C_{14}H_{13}As$	V
$C_{12}H_{18}OPd$	XIV, XVII	$C_{14}H_{13}MnO_2$	X, XVII
$C_{12}H_{20}Pt_2$	I	$C_{14}H_{14}F_6$	X
$C_{12}H_{20}Sn$	VI	$C_{14}H_{14}FeO$	XVIII
$C_{12}H_{22}Cl_2O_2Pd_2$	XIV	$C_{14}H_{14}FeO_2$	XVIII
$C_{12}H_{22}Br_2O_2Pd_2$	XIV	$C_{14}H_{14}FeO_4$	XVIII
$C_{12}H_{22}I_2O_2Pd_2$	XIV	$C_{14}H_{15}Fe$	XV
$C_{12}H_{24}F_2Si$	IX	$C_{14}H_{16}Cl_2Rh_2$	X
$C_{12}H_{24}GaN$	VI	$C_{14}H_{16}Fe$	XVII, XVIII
$C_{12}H_{26}F_2OSi_2$	IX	$C_{14}H_{16}Fe_2O_2S_2$	XVII
$C_{12}H_{27}Al$	III	$C_{14}H_{16}MoO_2$	XIV, XV, XVIII
$C_{12}H_{27}B$	III	$C_{14}H_{16}MoO_3$	XIX
$C_{12}H_{28}Li_2O$	III	$C_{14}H_{17}Fe_2O_2P$	XVII
$C_{12}H_{28}Pb$	III	$C_{14}H_{18}Fe$	XV
$C_{12}H_{28}Sn$	III	$C_{14}H_{20}F_2Si$	IX
$C_{12}H_{30}Al_2O_2$	I	$C_{14}H_{22}As_2Ni_2$	XVII
$C_{12}H_{36}Sn_6$	I	$C_{14}H_{22}Mo_2S_4$	XVII
$C_{12}H_{36}I_4Pt_4$	I	$C_{14}H_{22}N_2O_2Pd_2S_2$	XIV
$C_{13}F_6Mn_2O_{10}$	IV	$C_{14}H_{22}Ni_2P_2$	XVII

Formula	Table	Formula	Table
$C_{14}H_{22}OPd$	XIV, XVII	$C_{16}H_{20}NiO_2$	X
$C_{14}H_{22}O_4P_2W_2$	XVII	$C_{16}H_{22}As_2Fe_2O_2$	XVII
$C_{14}H_{26}Cl_2O_2Pd_2$	XIV	$C_{16}H_{22}Fe$	X, XVIII
$C_{14}H_{26}Br_2O_2Pd_2$	XIV	$C_{16}H_{22}Fe_2O_2P$	XVII
$C_{14}H_{26}I_2O_2Pd_2$	XIV	$C_{16}H_{22}Ru$	X
$C_{14}H_{27}F_5Sn$	IV	$C_{16}H_{24}Cl_2Rh_2$	X
		$C_{16}H_{30}Cl_2O_2Pd_2$	XIV
$C_{15}H_6D_2Fe_2O_5$	XVI	$C_{16}H_{32}O_4Pt_2$	I
$C_{15}H_6Mn_2O_{12}$	IV		
$C_{15}H_8Fe_2O_5$	XVI	$C_{17}H_{14}F_8FeO_3$	X
$C_{15}H_{11}MnO_3$	XVIII	$C_{17}H_{14}FeO$	XVII, XVIII
$C_{15}H_{14}Co_2$	XVII	$C_{17}H_{14}OO_8$	XVII
$C_{15}H_{14}Cr$	XVI, XVII	$C_{17}H_{14}ORh$	XVII
$C_{15}H_{15}Mn_2N_3O_3$	XVII	$C_{17}H_{16}Fe$	XVII, XVIII
$C_{15}H_{15}Rh$	XVII	$C_{17}H_{16}Fe_2O_4$	III, XVII
$C_{15}H_{16}Cr$	XV, XVII	$C_{17}H_{18}Fe_2O_2$	XVIII
$C_{15}H_{16}Fe$	XVIII	$C_{17}H_{20}FeO_4$	XVIII
$C_{15}H_{16}FeO$	XVIII	$C_{17}H_{20}NiO_2$	X
$C_{15}H_{16}FeO_4$	XVIII	$C_{17}H_{22}NiO_2$	X
$C_{15}H_{18}$	XVI		
$C_{15}H_{18}Fe$	XVIII	$C_{18}H_{10}O_8V_2$	XVII
$C_{15}H_{19}MnO_3$	XVIII	$C_{18}H_{14}Fe$	XVIII
$C_{15}H_{27}F_7Sn$	IV	$C_{18}H_{14}Fe_2O_4$	III
		$C_{18}H_{15}As$	VII
$C_{16}H_{10}F_8Sn$	VIII	$C_{18}H_{15}ClSi$	VII
$C_{16}H_{10}Fe_2O_5$	XVI	$C_{18}H_{15}ClSn$	VII
$C_{16}H_{10}HgMo_2O_6$	XVII	$C_{18}H_{15}P$	VII
$C_{16}H_{11}F_8O_6PW_2^+$	XVII	$C_{18}H_{15}Sb$	VII
$C_{16}H_{11}HgO_6W_2^+$	XVII	$C_{18}H_{15}Ti$	VII
$C_{16}H_{11}MoO_6W^+$	XVII	$C_{18}H_{16}Fe_2O_5$	III, XVII
$C_{16}H_{11}Mo_2O_6^+$	XVII	$C_{18}H_{16}Si$	VI
$C_{16}H_{11}O_6W_2^+$	XVII	$C_{18}H_{18}Co_2$	X, XVII
$C_{16}H_{12}D_2Fe$	XVIII	$C_{18}H_{18}Fe_2O_4$	III, XVII
$C_{16}H_{14}Fe$	XVIII	$C_{18}H_{18}Fe_2O_6$	XV
$C_{16}H_{14}FeO_3$	XVI	$C_{18}H_{18}Rh_2$	X
$C_{16}H_{14}I_3Rh$	XVII, XVIII	$C_{18}H_{19}Rh$	XVII
$C_{16}H_{15}Rh$	XVII	$C_{18}H_{20}Cr$	XVI, XVII
$C_{16}H_{16}Cl_2Rh_2$	X	$C_{18}H_{20}FeO$	XVIII
$C_{16}H_{16}FeO$	XVIII	$C_{18}H_{20}NiO_2$	X
$C_{16}H_{16}Mo_2O_4S_2$	XVII	$C_{18}H_{20}NiO_3$	X
$C_{16}H_{16}NiO_3$	XIV, XVII	$C_{18}H_{22}As_2Mo_2O_4$	XVII
$C_{16}H_{16}O_4S_2W_2$	XVII	$C_{18}H_{22}FeO_4$	XVIII
$C_{16}H_{16}Si$	V, VII	$C_{18}H_{22}Mo_2O_4P_2$	XVII
$C_{16}H_{17}Mo_2O_4P$	XVII	$C_{18}H_{22}Ni$	XIV, XVII
$C_{16}H_{18}Fe$	XVIII	$C_{18}H_{22}NiO_2$	X
$C_{16}H_{18}FeO_4$	XVIII	$C_{18}H_{24}NiO_2$	X
$C_{16}H_{20}Co_2O_4$	XV	$C_{18}H_{34}Cl_2O_2Pd_2$	XIV
$C_{16}H_{20}Fe$	XVIII	$C_{18}H_{34}I_2O_2Pd_2$	XIV

Formula	Table	Formula	Table
$C_{18}H_{37}ClP_4Ru$	VII	$C_{24}H_{12}Si$	VII
$C_{18}H_{38}P_4Ru$	VII	$C_{24}H_{19}FeO_2$	XVIII
$C_{19}H_{17}Co$	XV, XVII	$C_{24}H_{18}ORu$	XVII
$C_{19}H_{19}CoF_6$	X, XVII	$C_{24}H_{20}B$	VII
$C_{19}H_{20}FeO$	XVIII	$C_{24}H_{20}Sn$	VII
$C_{19}H_{20}Fe_2O_4$	III	$C_{24}H_{21}Fe_2O_2P$	XVII
$C_{19}H_{22}Fe$	XVIII	$C_{24}H_{22}Rh$	XVIII
		$C_{24}H_{46}O_4Pt_2$	I
$C_{20}H_{18}Fe_2$	XVII, XVIII	$C_{25}H_{21}FeO_2P$	XV
$C_{20}H_{18}Fe_2Hg$	XVII, XVIII	$C_{25}H_{24}Co_2$	XV
$C_{20}H_{18}Fe_2O_5$	XVI	$C_{26}H_{30}F_2Si$	IX
$C_{20}H_{18}Si$	V, VII	$C_{26}H_{30}Fe_2$	XVII, XVIII
$C_{20}H_{20}Mo$	XVII	$C_{26}H_{30}F_2GeSi$	IX
$C_{20}H_{20}Tc_2$	XVII	$C_{27}H_{26}Co_3P$	XIV
$C_{20}H_{20}Th$	XVII	$C_{28}H_{23}AsFeO_2$	XV
$C_{20}H_{21}Tc_2^+$	XVII	$C_{28}H_{23}FeO_2Sb$	XV
$C_{20}H_{22}Fe_2N_2O_4$	XVIII	$C_{28}H_{28}CoO_3P$	XIV
$C_{20}H_{22}Fe_2O_4$	III	$C_{30}H_{30}Mn_6N_8O_8$	XVII
$C_{20}H_{24}NiO_2$	X	$C_{31}H_{22}FeO_3$	XV
$C_{20}H_{24}NiO_4$	X	$C_{32}H_{28}Pt_2$	VII
$C_{20}H_{40}O_4Pt_2$	I	$C_{34}H_{30}Ni_2P_2$	XVII
$C_{21}H_{20}ClNiP$	XIII	$C_{36}H_{30}Fe_2O_2P_2$	XVII
$C_{21}H_{24}FeO$	XVIII	$C_{40}H_{30}As_2F_6Pt$	IX
$C_{22}H_{14}Fe_2O_{10}$	XV	$C_{40}H_{30}F_6P_2Pt$	IX
$C_{22}H_{14}Fe_2O_6$	XV		
$C_{22}H_{20}Co_2F_4$	XV		
$C_{22}H_{22}Fe_2$	XVII		
$C_{22}H_{22}Fe_2$	XVIII		
$C_{22}H_{28}Fe_2N_2O_4$	I, XVIII		

Lewis Base-Metal Carbonyl Complexes

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I

INTRODUCTION

The chemistry of the metal carbonyls has been the subject of hundreds of research papers, most of them appearing in the last decade of "renaissance" of inorganic chemistry. Reviews have appeared on the metal carbonyls themselves (1, 2) and on such related topics as the anionic carbonyl-metallates (3), metal-olefin complexes (4, 5), tricarbonyl(diene)iron species (6), perfluoroalkyl metal compounds (7), and π -cyclopentadienyl and π -arene (8, 9) metal derivatives.¹

The intent of this article is to focus upon compounds of transition metals bonded to carbonyl groups as well as to other electron-donating groups. Most of these substances involve coordinate bonds from atoms of the fifth

¹ A comprehensive review of alkali metal derivatives of metal carbonyls by R. B. King appeared in Volume 2 of *Advances in Organometallic Chemistry*.

and sixth main groups of the periodic table, but because of the multiplicity of species involved, it has not proven convenient to adhere to a strict definition of the topic as "Lewis base-metal carbonyl complexes." In the absence of other Lewis bases such compounds as the carbonyl hydrides, halides or cyanides, cyclopentadienyl, arene, olefin, and acetylene complexes, alkyl and acyl derivatives, and carbonylmetallates are beyond the scope of this review.

Broad agreement appears to have existed for some time as to the principles governing the formation, structure, and properties of metal carbonyl derivatives. Since there appears to be no need to repeat in detail what is well summarized in earlier reviews (1, 2, 10), the next section of this article attempts only to limn broadly the rules and correspondences which are widely cited in papers in the area. Emphasis will be placed upon the generalizations which provide the strands weaving together the chemistry of many compounds into a manageable fabric. Subsequent sections summarize the compounds involved, element by element. In the interests of brevity, clarity, and quick comprehension, in most cases formulas and common abbreviations are used, rather than systematic names.

II

GENERAL CONSIDERATIONS

A. Effective Atomic Number Rule

Foremost among the long-recognized regularities of the chemistry of the metal carbonyls is the adherence of the vast majority of compounds to the "effective atomic number" or "rare-gas" rule. That is, the central metal atom accepts a number of additional electrons furnished by the ligands, so that the total number of electrons surrounding the metal gives it a formally closed-shell configuration. Species not conforming to the rule are well known but still few enough to be acknowledged as "exceptions." The arbitrary bookkeeping scheme utilized has been remarkably, even if fortuitously, successful in predicting and correlating the stoichiometries of complexes. For instance, in pentacarbonyliron the zero-valent iron atom, having 26 electrons, is said to accept two electrons from each of five carbonyl groups, thus gaining a 36-electron (krypton) configuration.

The system is applied similarly when more than one type of ligand is present. It should be noted that one may regard many compounds in at

least two ways for the electron-counting procedure. Thus, the compound $[\text{FeI}_2(\text{CO})_4]$ may be considered to be composed of $\text{Fe}(0)$ (26 electrons), two iodine radicals (2×1 electron), and the carbonyl groups (4×2 electrons); or of $\text{Fe}(\text{II})$ (24 electrons), two iodide anions (2×2 electrons), and the carbonyl groups (4×2 electrons). In either case there is no net charge on the complex, and the total number of electrons is 36. The apparent difference in formal oxidation state of the central atom has little real meaning in most cases. Table I lists some of the more common donor groups, arranged according to the number of electrons formally donated by them.

TABLE I
ELECTRON DONORS

Number of electrons	Donor groups
One	$\cdot\text{H}$, $\cdot\text{Cl}$, $\cdot\text{Br}$, $\cdot\text{I}$, $\cdot\text{CH}_2\text{R}$, $\cdot\text{COR}$, $\cdot\text{CF}_2\text{R}$, $\cdot\text{SnR}_3$
Two	CO , NR_3 , PR_3 , AsR_3 , SbR_3 , OR_2 , SR_2 , Cl^- , Br^- , I^- , CN^- , H^-
Three	NO , $\cdot\text{PR}_2$, $\cdot\text{AsR}_2$, $\cdot\text{SR}$

The coordination number of the metal atom is influenced by the way in which electron-donating groups satisfy the rare-gas rule. Thus, 36-electron species exist for iron with coordination numbers of four (dicarbonyldinitrosyliron), five (pentacarbonyliron), and six (diiodotetracarbonyliron). Of course, the configuration, bonding, and modes of reaction are influenced by the coordination number of the central atom in a complex.

Polynuclear species, in particular binuclear ones, are common among the metal carbonyls and their derivatives. In the simplest instances, e.g., decacarbonyldimanganese, the only interaction between the two "halves" of the complex is a metal-metal bond; and in others, e.g., octacarbonyldicobalt, the bonding also involves "bridging" carbonyl groups, which are shared by both metal atoms (2). Bidentate donors can act as bridges, as in $[(\text{CO})_4\text{FeP}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_2(\text{C}_6\text{H}_5)_2\text{PFe}(\text{CO})_4]$ (11, 12). In certain species, e.g., $[\text{FeS}(\text{CO})_3]_2$ (13) and $[\text{Fe}(\text{C}_5\text{H}_5)\text{P}(\text{CH}_3)_2\text{CO}]_2$ (14), other groups link the halves of the complex. The bridged structures are usually consistent with the rare-gas rule, if one assigns to each of two metal atoms so joined one-half of the number of electrons which that ligand would donate to one acceptor atom. It should be pointed out that certain common bridging

groups, such as $\text{RS}\cdot$ and $\text{R}_2\text{P}\cdot$, are radicals, often derived by cleavage of an initial reagent, in these cases possibly a dialkyl disulfide or tetraalkylbiphosphine. (Alternatively they are anions, $[\text{RS}]^-$ and $[\text{R}_2\text{P}]^-$, donating four instead of three electrons.) The metal-metal interaction may be approached by a consideration of central metal atoms of odd atomic number in the light of the rare-gas rule. Clearly, a whole number of pair-donating ligands can complete the electron shell of an atom of even atomic number, as is exemplified by the cases of the simple carbonyls of chromium, iron, and nickel. However, such atoms as manganese(0) (25 electrons) and cobalt(0) (27 electrons) must receive one electron in addition to those furnished in pairs. This requirement may be satisfied by the sharing of the odd electron on each atom with another such atom, thus giving a metal-metal bond, as in $[\text{Co}_2(\text{CO})_8]$ and $[\text{Mn}_2(\text{CO})_{10}]$. Other bridging groups may or may not be present, as in the former and the latter cases, respectively. In these substances the presence of a metal-metal bond produces diamagnetism, whereas absence of the metal-metal bond would cause paramagnetism. Thus, magnetic susceptibility provides a ready test for the presence of metal-metal interactions in compounds of appropriate stoichiometry, provided one knows of the presence or absence of other bridging groups. This frequently is, in effect, a test for a monomeric or dimeric species, as in the case of $[\text{Mn}(\text{CO})_4\text{PR}_3]_{1 \text{ or } 2}$ (15). Evidence for metal-metal bonds from X-ray crystallographic studies is also well established (16).

The donation of an odd number of electrons from another ligand may remove the need to suggest a metal-metal bond for atoms of odd atomic number and may require such a proposal for compounds of elements of even atomic number. Thus, tricarbonylnitrosylcobalt is a monomeric, diamagnetic compound. On the other hand, a metal-metal bond must be postulated to explain the diamagnetism of the group of compounds of composition $[\text{FeSR}(\text{CO})_3]_2$ (13) [$\text{Fe}(0) + 3\text{CO} + \text{SR} \rightarrow 26 \text{ electrons} + 3 \times 2 \text{ electrons} + 3 \text{ electrons} = 35 \text{ electrons}$]. An X-ray study of the structure of $[\text{Fe}(\text{SC}_2\text{H}_5)(\text{CO})_3]_2$ has verified this proposal (16). Monomeric complex species with an over-all charge may also satisfy the rare-gas rule or at least attain diamagnetism. Thus, the metal atoms in the anions $[\text{Mn}(\text{CO})_5]^-$ and $[\text{Co}(\text{CO})_4]^-$ (1, 2) and the cation $\{\text{Co}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+$ (17) all have "attained" the krypton configuration.

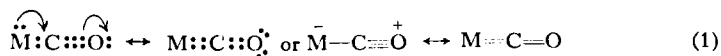
Consideration of the effective atomic number rule and the determination of coordination number by the electron-donating properties of ligands has led to the arranging of compounds in isostructural and/or isoelectronic

series, the members of which are often very similar in certain respects. The tetracoordinate groups of varying charge, $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Co}(\text{CO})_4]^-$, and $[\text{Ni}(\text{CO})_4]$, exemplify one form of such a series. Another series of "pseudonickel carbonyls" is composed of $[\text{MnCO}(\text{NO})_3]$, $[\text{Fe}(\text{CO})_2(\text{NO})_2]$, $[\text{Co}(\text{CO})_3(\text{NO})]$, and $[\text{Ni}(\text{CO})_4]$ (18). The similarity in reactivity between a metal carbonyl and the cyclopentadienyl carbonyl one place to the left in the periodic table, e.g., $[\text{Co}(\text{CO})_4]_2$ and $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$, has been noted (19). Many other such series may be constructed. The treatment of compounds related in these ways with bases frequently results in equivalent reactions.

B. Nature of the Bonding

1. The Carbonyl Group

Leaving aside the systematics of stoichiometry in metal carbonyl derivatives, one must consider the nature of the metal-ligand bond. Detailed discussions of the carbon-oxygen and metal-carbon bonds in the metal carbonyls have been given (10, 20) and reviewed (1, 2) in the past. We limit ourselves here to the generally accepted, qualitative conclusions. The carbon atom of a carbonyl group possesses an essentially sp -hybrid lone pair of electrons. Although this lone pair shows virtually no sign of basicity, it is responsible for forming a σ -coordinate bond by overlap with a vacant transition metal hybrid orbital of the proper symmetry. The carbonyl group has in addition fairly low-lying π -antibonding orbitals, which overlap with filled nonbonding d orbitals of appropriate symmetry on the metal atom, thus forming a π bond. The σ bond, donating electron density to the metal, and the π bond, removing electron density from the metal atom, provide a means for avoiding charge separation in the molecule as a whole and interact "synergically" to strengthen one another. This combination of donor and acceptor properties gives carbon monoxide its remarkable power as a ligand for atoms with partly filled d -electron shells. The metal-carbon bond order in transition metal carbonyls, then, is expected to be greater than one. In valence-bond terms, since a carbon monoxide group with a triple bond between carbon and oxygen can form only a single bond between a metal and carbon, any metal-carbon double bonding must be accompanied by a decrease in the carbon-oxygen bond order. This may be expressed by the simple resonance picture [Eq. (1)]



2. Other Ligands and the Metal Atom

Most other ligands which are found in substituted metal carbonyls also possess both σ -donor and π -acceptor properties. Some, including amines and ethers, which bond through first-row atoms lacking suitable low-lying empty orbitals, can function only as donors. Usually, these form less robust metal carbonyl derivatives than the ligands having some double-bonding properties. The acceptor abilities of such compounds as phosphines and arsines arise from empty d orbitals on the phosphorus or arsenic atoms. Nitrogen atoms in unsaturated heterocyclic compounds, such as 2,2'-dipyridyl, also possess acceptor properties. It will be recognized that the ligands most favorable for carbonyl complex formation are the class B ligands of Ahrland *et al.* (21). Generally, these other ligands are better σ donors (more basic) but poorer acceptors than the carbonyl groups they replace. The order of σ -donor power of ligands may be determined by well-known methods independent of transition metal coordination chemistry. The arrangement of ligands according to their π -acceptor properties by infrared measurements is discussed in a later section.

Since the metal atoms under consideration accept σ donation into empty orbitals and utilize filled d orbitals for π back-bonding, the electron density on any metal atom must give it a certain capacity for both σ and π bonding, in other words, a specific double-bonding ability. This effective electron density is determined initially by the position of the atom in the transition series and its valence state. However, considerations of symmetry may limit the formation of π bonds (20, 22).

The number of electrons in nonbonding d orbitals after the metal atom has accepted the σ electrons from the ligands restricts the maximum number of π bonds that can be formed, even if the symmetry requirements are met. Clearly, the presence of positive charge on an atom increases its acceptor ability and decreases its back-bonding ability; the opposite effects are produced by negative charge. As double bonding appears essential for the formation of the carbonyls and their derivatives, most of these compounds are found in low valence states.

3. Competition between Ligands

Since the ligands must in effect compete for the limited bonding potentialities of the central atom, the bonding between a metal atom and any one molecule must be affected by the nature of the other groups present. In this way the stability of a given metal-ligand bond or a given complex depends

upon the interaction of the σ - and π -bonding capabilities of the various ligands and the metal atom. For instance, in a hexacoordinate system, chromium(0), having accepted six pairs of electrons in σ bonds, has six electrons in d orbitals available for back-bonding (three possible double bonds). Distributed among six ligands of identical bonding tendencies, as in $\text{Cr}(\text{CO})_6$, the electrons are sufficient for a maximum metal-carbon bond order of 1.5. However, as carbonyl groups are replaced by ligands, such as phosphines, which are less-capable acceptors, the "double-bond character" may become more concentrated in the remaining metal-carbon bonds; here the hypothetical maximum metal-carbon bond order of 2.0 would occur in a complex of type $[\text{Cr}(\text{CO})_3\text{L}_3]$, in which L had no double-bonding propensity. This sort of effect, in reality a delicate compromise among many factors in each case, is observed not only in the matter of "stability," but in infrared spectra and reaction mechanisms as well. These frequently stated concepts (1, 2, 20), superficially presented here, of the rare-gas rule and the possibility of metal-ligand double bonding, for which the various ligands compete, provide a framework into which one can fit much of the extensive experimental data on the metal carbonyl-base complexes.

C. Infrared Spectra

The infrared spectrum is doubtless the most widely reported feature of metal carbonyl complexes, aside from their composition. One of the factors making carbonyl chemistry an attractive field for a multitude of investigators in recent years has been the ease of monitoring reactions, identifying fractions, and detecting purity or the lack thereof by infrared spectroscopy. In addition to providing a means for distinguishing one compound from another and for recognizing structural similarities in groups of compounds, the infrared spectrum aids in estimating degrees of double bonding and molecular symmetry. Many of our data and concepts regarding the bonding in carbonyl complexes have been obtained from infrared spectroscopic studies. In fact, many of the reported carbonyl complexes have been prepared primarily for the sake of their infrared spectra.

A general discussion of the infrared spectra of transition metal complexes has been published (23). Although correlations of CO bending modes (24) and of band intensities (25, 26) have appeared and vibrations of other ligands are often noted, the number of CO stretching modes and their exact frequencies are the data most frequently cited for metal carbonyl com-

pounds. Experimentally, the effect of solvent upon band resolution and position must be taken into account (27, 27a); the most favorable solvents are generally saturated hydrocarbons, e.g., cyclohexane (27a). The sodium chloride prisms commonly found in infrared spectrophotometers may easily give misleading results; reliable data should be obtained with higher-resolution instruments utilizing gratings, or fluorite or lithium fluoride prisms (23).

The symmetry properties of a molecule, which may be established for any given structure, determine the number (and type) of infrared-active vibrational modes which are expected for the vibrating groups (22). It is

TABLE II
INFRARED-ACTIVE CARBONYL VIBRATIONS IN OCTAHEDRAL
COMPLEXES

Structure	Symmetry	Vibrations	Number
$[\text{M}(\text{CO})_5\text{L}]$	C_{4v}	$2A_1 + E$	3
<i>cis</i> - $[\text{M}(\text{CO})_4\text{L}_2]$	C_{2v}	$2A_1 + B_1 + B_2$	4
<i>trans</i> - $[\text{M}(\text{CO})_4\text{L}_2]$	D_{4h}	E_u	1
<i>cis</i> - $[\text{M}(\text{CO})_3\text{L}_3]$	C_{3v}	$A_1 + E$	2
<i>trans</i> - $[\text{M}(\text{CO})_3\text{L}_3]$	C_{2v}	$2A_1 + B_1$	3
<i>cis</i> - $[\text{M}(\text{CO})_2\text{L}_4]$	C_{2v}	$A_1 + B_1$	2
<i>trans</i> - $[\text{M}(\text{CO})_2\text{L}_4]$	D_{4h}	A_{2u}	1
$[\text{M}(\text{CO})\text{L}_5]$	C_{4v}	A_1	1

customary in these predictions to regard the ligands as points, so that the over-all symmetry of the coordination polyhedron is considered. One sometimes observes coincidences of bands which should be separated and splittings of bands which should not be split; the latter phenomenon is often caused by the local symmetry of ligands, which were treated as points in the original calculation. Bearing these pitfalls in mind, one may frequently deduce the molecular configuration from the number of CO stretching vibrations. In practice this technique has been used quite extensively and successfully, the results being found in a multitude of papers dealing with the preparation of new complexes.

We cite here a few papers particularly concerned with the analysis of infrared spectra, which summarize many data and present coherently the necessary reasoning (28-34b). The problem of assignment of a given band

to a vibration of a given symmetry type has been attacked through the use of arguments based on relative intensities (28) or local oscillating dipoles (34), or by more powerful methods based on assumptions regarding the CO stretching force constants and their interactions (29, 31, 32, 33).

Although complexes of various coordination numbers have been studied, those with an octahedral metal atom, including substituted Group VI carbonyls and manganese carbonyl halides and their derivatives, have been

TABLE III
INFRARED-ACTIVE CARBONYL VIBRATIONS IN TETRACOORDINATE COMPLEXES

Structure	Symmetry	Vibrations	Number
[M(CO)₃L]			
Tetrahedral	C_{3v}	$A_1 + E$	2
Square planar	C_{2v}	$2A_1 + B_1$	3
[M(CO)₂L₂]			
Tetrahedral	C_{2v}	$A_1 + B_1$	2
<i>cis</i> -Square planar	C_{2v}	$A_1 + B_1$	2
<i>trans</i> -Square planar	D_{2h}	B_{2u}	1
[M(CO)L₃]			
Tetrahedral	C_{3v}	A_1	1
Square planar	C_{2v}	A_1	1

most intensively analyzed. The octahedral system lends itself well to these treatments, since to a first approximation symmetry allows no mixing of the orbitals used in σ bonding (d_{z^2} , $d_{x^2-y^2}$, s , p_x , p_y , p_z) with those used in π bonding (d_{xy} , d_{yz} , d_{zx}) (31). Tables II, III, and IV summarize the infrared-active carbonyl vibrations for the various hexa- (28, 29, 31), tetra- (30), and pentacoordinate (35) structures. It should be obvious that the same results apply for bond-stretching frequencies of other ligands, e.g., the CN frequency in isonitrile derivatives (35) or the NO frequency in nitrosyls (36).

The CO stretching frequencies of metal carbonyl compounds are found between about 2150 and about 1650 cm^{-1} ; absorption below about 1850 cm^{-1} is often indicative of bridging carbonyl groups, but the presence of ligands without π -acceptor properties, e.g., amines, may force terminal

carbonyl frequencies into this region (2, 32, 37). The CO stretching frequency depends upon the CO bond order, which in turn reflects metal-carbon double bonding, itself dependent upon the nature of other ligands present. Thus, the effect upon the CO frequency of replacing a carbonyl group by another ligand is a measure of the π - and σ -bonding capabilities of the ligand. Indeed, this is one of the main sources of our ideas regarding

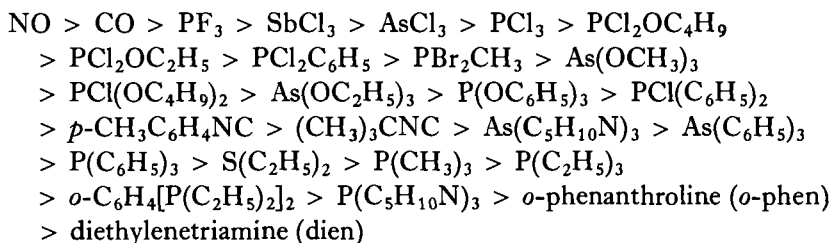
TABLE IV
INFRARED-ACTIVE CARBONYL VIBRATIONS IN PENTACOORDINATE COMPLEXES

Structure	Symmetry	Vibrations	Number
[M(CO) ₄ L]			
Axial rectangular pyramid	C_{4v}	$A_1 + E$	2
Equatorial rectangular pyramid	C_s	$3A' + A''$	4
Axial trigonal bipyramid	C_{3v}	$2A_1 + E$	3
Equatorial trigonal bipyramid	C_{2v}	$2A_1 + B_1 + B_2$	4
[M(CO) ₃ L ₂]			
<i>trans</i> -Rectangular pyramid	C_{2v}	$2A_1 + B_1$	3
<i>cis</i> -Rectangular pyramid	C_s	$2A' + A''$	3
<i>trans</i> -Trigonal bipyramid	D_{3h}	E'	1
<i>cis</i> -Trigonal bipyramid	C_{2v}	$2A_1 + B_1$	3
	C_s	$2A' + A''$	3
[M(CO) ₃ L ₃]			
<i>trans</i> -Rectangular pyramid	C_{2v}	$A_1 + B_2$	2
<i>cis</i> -Rectangular pyramid	C_s	$2A'$	2
<i>trans</i> -Trigonal bipyramid	D_{3h}	A_2''	1
<i>cis</i> -Trigonal bipyramid	C_{2v}	$A_1 + B_2$	2
	C_s	$A' + A''$	2
[M(CO)L ₄]	Any	—	1

the π -bonding tendencies of ligands (33, 36). Almost every paper devoted to metal carbonyl complexes comments upon the effect of substitution upon the CO stretching frequency. An additional influence is that of charge. In the isoelectronic, isostructural series $[\text{Fe}(\text{CO})_4]^{2-}$, $[\text{Co}(\text{CO})_4]^-$, $[\text{Ni}(\text{CO})_4]$, the CO frequency rises in the sequence 1786, 1887, 2057 cm^{-1} (38); the lower the negative charge, the lower the metal-carbon bond order, the higher the carbon-oxygen bond order, and the higher the CO frequency.

Electronegative substituents, such as halide ions or perfluoroalkyl groups, may raise the CO frequency above that in the unsubstituted carbonyls (39). Lewis bases on the other hand, being less good π acceptors than carbon monoxide, lower the CO frequency when they replace carbonyl groups (31). The greater the degree of substitution, the greater the shift in frequency (29, 30, 31, 36).

From the magnitudes of these effects orders of ligands with respect to π bonding may be compiled. A recent article (36), combining new measurements with literature data, describes a series of ligands in descending order of π -acceptor ability:



The inductive and mesomeric effects of substituents upon the donor atom clearly must influence both its donor and acceptor properties (30, 37, 40, 41). It is interesting to note that despite differences in their reactivity and the stability of their derivatives, the donor atoms sulfur, phosphorus, and arsenic (in comparable sulfides, phosphines, or arsines) appear to have essentially the same double-bonding capacity (42–45). Antimony and bismuth resemble arsenic and phosphorus in this respect (46). It has been suggested that isocyanides have equivalent σ -donor power but much less π -acceptor power than carbonyl groups (47, 48, 49). Nitrogen in amines and oxygen in ethers have virtually no π -acceptor properties (33). The donor-acceptor properties of the ligands are not constant, but vary with the nature of the central atom and its environment (49, 50, 51). Thus, although pyridine has some π -acceptor ability, it is purely a donor in the complexes $[\text{M}(\text{CO})_5\text{py}]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), in which the five carbonyl groups accept all the available electron density; in the disubstituted compounds $[\text{M}(\text{CO})_4(\text{py})_2]$, the pyridine does accept electrons (32).

When both NO and CO are found in a molecule, as in $[\text{Co}(\text{CO})_3\text{NO}]$, replacement of carbonyl groups by phosphines affects the stretching frequencies of the remaining CO and NO groups. In a low electron density

situation, NO and CO appear to be about equal in π -acceptor properties; in circumstances of higher electron density, NO seems to be somewhat the better acceptor of the two (36). Application of force constant calculations rather than just frequencies to the estimation of π -bonding abilities has verified some of the qualitative conclusions (30, 33, 47, 48) and yielded some further ones (38). Phosphorus trifluoride is found to be a stronger π acceptor even than CO. Acetonitrile possesses slight acceptor ability. Quite remarkably, dimethylformamide and methylformamide appear to be π donors rather than acceptors (33). Not all of the CO bands of a molecule are shifted to the same extent by substitution. When CO stretching frequencies are assigned, the effect of a ligand upon the frequencies of CO groups in specific geometric relationships to the ligand may be measured. It is found that in octahedral complexes a ligand affects most strongly the CO groups *trans* to it (28, 31, 52, 53).

A dissent has been entered to some of the views on π bonding and CO stretching frequencies. The CO stretching frequency in complexes of the type $[\text{Ni}(\text{CO})_{4-n}(\text{PR}_3)_n]$ is a linear function of the polar constant σ^* of the group R. It has been concluded that the π -acceptor property of PF_3 is essentially equal to that of PR_3 , both being very small. The phenomenon of CO stretching frequency variation is alleged to be due predominantly to differences in the σ -bonding capacity of the ligands (41).

D. Reaction Mechanisms

Although their number is steadily increasing, relatively few studies of reaction mechanisms have been concerned with metal carbonyl derivatives. Two methods are commonly employed to study the kinetics—exchange of radioactive carbon monoxide and infrared spectroscopy. The results of these investigations, which are discussed in the element-by-element survey, are satisfactorily explained in most cases by the familiar concepts of metal-ligand double bonding. Papers in this area have dealt with phosphine exchange in nickel carbonyl complexes (40); the carbon monoxide exchange of metal carbonyls (54), phosphine-substituted nickel carbonyls (55), metal carbonyl halides (56), $\{\text{RhCl}_3\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (57), and $\{\text{RhClCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (58); the acid-induced carbon monoxide exchange of iron pentacarbonyl and its triphenylphosphine complexes (59); the isomerism of disubstituted manganese pentacarbonyl bromide (60, 61); the reactions between man-

ganese pentacarbonyl halides (62) or their monosubstituted derivatives (63) and bases; and the reactions between triphenylphosphine and acyl (64), π -allyl (65), and other (66) derivatives of cobalt carbonyl. The great majority of these reactions proceed by dissociative mechanisms. Studies of the direct reaction between Group VI hexacarbonyls and ligands are discussed in Section III, C.

E. Other Physical Techniques

Other physical techniques have been applied less extensively than infrared spectroscopy. Dipole moments are frequently employed to determine configurations and charge transfer in bonds. Proton nuclear magnetic resonance spectra have been used to detect protonated species (67, 68) and have been of great utility in showing the existence and nature of isomers of certain bridged complexes, e.g., $[\text{Fe}(\text{SCH}_3)(\text{CO})_3]_2$ (69) and $[\text{Mo}(\text{C}_5\text{H}_5)\text{P}(\text{CH}_3)_2(\text{CO})_2]$ (70). In such cases the hydrocarbon groups may be in equivalent or nonequivalent positions, depending upon the molecular configuration. The environment is, of course, reflected in the degree of simplicity and symmetry of the NMR pattern. The presence and relative magnitude of P—P coupling in complexes of tris(dimethylamino)phosphine has been inferred from the shape of the methyl resonances. This work suggests that P—P coupling is significant between phosphorus atoms only if they are *trans* to one another in octahedral or trigonal bipyramidal complexes (71).

Phosphorus-31 NMR spectra have been reported for a number of nickel carbonyl complexes and some qualitative correlations have been drawn concerning the Ni—P bond order (72). The use of magnetic susceptibility measurements has already been mentioned. Most metal carbonyl complexes are diamagnetic, however. Mössbauer effect studies of iron carbonyl and its derivatives have included base-substituted compounds (73, 74, 75). Workers have constructed a table of additive partial isomer shift values for a number of ligands, finding that lone pair donors with negligible π -acceptor power have essentially zero effect on the isomer shift, whereas π -bonding ligands do contribute significantly (73). The isomer shift is identical for the *cis* and *trans* isomers of $[\text{Fe}(\text{C}_5\text{H}_5)\text{P}(\text{CH}_3)_2(\text{CO})_2]$ and its arsenic analog (75). Single-crystal X-ray studies, which have confirmed crucial concepts of the structure and bonding in metal carbonyls and their derivatives, are mentioned in later sections where appropriate.

III

SURVEY OF REPORTED COMPOUNDS

A. *Common Aspects*

Since the synthetic approach has dominated much of the work in the area covered by this review, of many compounds little more may be said than that they exist. The remainder of this article surveys the compounds reported, with emphasis upon the methods of preparation. Where structures are indicated, unless it is otherwise remarked, one may assume that infrared spectroscopy and possibly dipole moment studies or NMR spectroscopy have provided the evidence for the formulation. It hardly seems necessary to repeat these phrases in every case. Unless designated as paramagnetic, the complexes are diamagnetic. The vast majority obey the rare-gas rule.

Among methods of preparation, the direct reaction between a metal carbonyl and the ligand has been by far the most common. The effects upon this approach of solvent, temperature, and ultraviolet irradiation are profound. Indirect synthetic methods have been employed in a number of cases. Relatively little is known about subsequent reactions of most of the complexes, save oxidation and ligand exchange. Oftentimes the only chemical property reported for these compounds is an ill-defined "stability," which usually refers to the abandon with which they may be handled in the ordinary laboratory. The compounds are usually solids, white, yellow, orange, or red in color, although other colors are sometimes seen. When the molecular weight is low enough, the nonionic species are sublimable. Sublimation, chromatography, and crystallization are the ordinary methods of purification. In the section on infrared spectroscopy the order of ligands according to π -acceptor properties has been discussed. For any metal atom there seems to be some especially stable combination of ligands, balanced according to their σ - and π -bonding capacities and those of the metal. As a group, tertiary phosphines form the greatest number of stable complexes; chelation confers extra stability. Steric as well as electronic effects may limit the extent of reactions and influence configurations. As discussed before, the strength of the remaining metal-carbon bonds is normally increased by the introduction of ligands other than carbon monoxide, so successive replacements of CO become progressively more difficult. Only rarely can all of the CO in a molecule be displaced directly. One is tempted to conclude that any combination of ligands may appear in a metal carbonyl complex

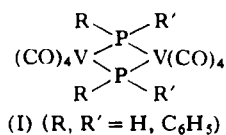
and that devising a suitable method of synthesis is the sole problem. The following pages may be construed as evidence for this hypothesis.

B. Vanadium

The paramagnetic hexacarbonylvanadium is the only unsubstituted carbonyl known of a Group V element. Because the compound is one electron short of the krypton configuration, it is very easily reduced to the $[\text{V}(\text{CO})_6]^-$ anion. Valence changes also occur easily, when carbonyl groups are replaced by other electron-pair-donating ligands. Reactions of $\text{V}(\text{CO})_6$ with nitrogen and oxygen donors (76, 77), triphenylphosphinemethylene (77) and triphenylphosphineimine (77) lead to disproportionation to products having no mixed base-carbonyl ions. Triphenylphosphine in ether also causes disproportionation of the hexacarbonyl, giving the substituted anion $[\text{V}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3]^-$, but in benzene these reagents lead to the zero-valent $\{\text{V}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (76). In hexane as well, triphenyl-, triethyl-, and tripropylphosphine lead to the paramagnetic *trans*- $[\text{V}(\text{CO})_4(\text{PR}_3)_2]$ species (78, 79). However, tricyclohexylphosphine under the same conditions gives a diamagnetic tetracarbonylbis(phosphine) compound, shown by infrared to exist in solution in a monomer-dimer equilibrium (78). The cyclohexyl compound is the most basic phosphine, with the least π -acceptor power, so excess negative charge accumulates on the vanadium atom, and dimerization represents a way of distributing this charge (78). The tetracarbonylbis(triphenylstibine) and -(triphenylarsine) compounds of vanadium, though observed, cannot be isolated (79). The chelating ligand *o*-phenylenebis(dimethylarsine) (diarsine) reacts with $[\text{V}(\text{CO})_6]$ to give a dimer $[\text{V}(\text{CO})_4(\text{diarsine})]_2$ which is converted by iodine into the heptacoordinate species $[\text{VI}(\text{CO})_4(\text{diarsine})]$ (79a).

Treatment of $\{\text{V}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ with sodium amalgam leads to the replacement of phosphine by carbon monoxide, forming the $[\text{V}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3]^-$ anion (76, 79); acidification then gives the hydride $[\text{VH}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3]$ (76) which is less acidic than $[\text{VH}(\text{CO})_6]$ itself (77). Thus the triphenylphosphine, a poorer acceptor than carbon monoxide, has made the central atom more basic.

Phosphine, phenylphosphine, or diphenylphosphine and $[\text{V}(\text{CO})_6]$ in



hexane give the compounds (I) with loss of hydrogen. In the case of diphenylphosphine, in the absence of solvent one may observe $[\text{V}(\text{CO})_4 \text{P}(\text{C}_6\text{H}_5)_2\text{H}]$, typical of the intermediates in the synthesis of the bridged compounds (78). Vanadium hexacarbonyl and nitric oxide give no stable products (76, 80), but tetracarbonylbis(triphenylphosphine)vanadium reacts with nitric oxide to give the stable, diamagnetic $[\text{V}(\text{CO})_4(\text{NO}) \text{P}(\text{C}_6\text{H}_5)_3]$ (80). Frequently (triphenylphosphine)(nitrosyl) carbonyls are more stable than simple nitrosyl carbonyls.

C. Chromium, Molybdenum, and Tungsten

1. *The Direct Reaction between the Carbonyls and Bases*

The reactions between the Group VI hexacarbonyls and Lewis bases have been extensively investigated. Contributing to the interest of so many workers have been the commercial availability of the carbonyls, their considerable stability and that of many of their derivatives, and the suitability of a hexacoordinate system for application of theory to results. Ligands bonding through nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, and sulfur have given Group VI metal carbonyl derivatives, most of which have been isolated, although some have been detected only spectroscopically, particularly the oxygen-bonded species. The great majority of these complexes have been prepared by the direct reaction of the ligand with the carbonyl, initiated either thermally or by ultraviolet light. However, with monodentate ligands it is often difficult to replace more than two carbonyl groups directly. A fruitful method for securing the more highly substituted compounds is the treatment of a tricarbonyl(arene)metal complex with the ligand. Other indirect methods, including ligand exchange, have been used. Table V lists the simple substitution products $[\text{M}(\text{CO})_{6-n}\text{L}_n]$ which have been reported for the carbonyls of chromium, molybdenum, and tungsten. To simplify the format, one molecule of chelating bidentate or tridentate ligand is referred to as L_2 or L_3 ; species bridged by bidentate ligands are called "binuclear."

The ultraviolet-light-initiated reaction of bases with the hexacarbonyls has been carefully studied by Strohmeier and his group (88, 89, 90, 92, 96, 99, 104, 105, 133-139a). It has been shown that the hexacarbonylmetal is excited and loses carbon monoxide to give a pentacarbonylmetal intermediate, which is rapidly attacked by a donor molecule (134, 137). The quantum yield is one for the preparation of the monosubstituted com-

TABLE V
SIMPLE SUBSTITUTION PRODUCTS OF THE GROUP VI HEXACARBONYLS^a

Ligand	Metal	[M(CO) ₅ L]	[M(CO) ₄ L ₂]	[M(CO) ₃ L ₃]	[M(CO) ₂ L ₄]
NH ₃	Cr	81	—	81, 83, 86	—
	Mo	82	—	81, 82, 84	—
	W	82	—	81, 82, 85	—
C ₆ H ₁₁ NH ₂	Cr	32	—	—	—
	Mo	32	—	—	—
	W	32	—	—	—
C ₆ H ₅ NH ₂	Cr	87, 88	—	—	—
	W	89	—	—	—
<i>p</i> -H ₂ NC ₆ H ₄ NH ₂	Cr	87, 91	— 90	—	—
	Mo	91		—	—
	W	82		—	—
<i>m</i> -H ₂ NC ₆ H ₄ NH ₂	Cr	87 binuclear	—	—	—
<i>o</i> -H ₂ NC ₆ H ₄ NH ₂	Cr	87	—	—	—
<i>s</i> -C ₆ H ₃ (NH ₂) ₃	Cr	87	—	—	—
C ₆ H ₁₀ (NH ₂) ₂	Cr	87	—	—	—

TABLE V—continued

Ligand	Metal	[M(CO) ₅ L]	[M(CO) ₄ L ₂]	[M(CO) ₃ L ₃]	[M(CO) ₂ L ₄]
(C ₂ H ₅) ₃ N	Cr	92	—	—	—
	W	92	—	—	—
C ₅ H ₁₀ NH (piperidine)	Cr	92	92	—	—
	Mo	92	92	—	—
	W	92	92	—	—
H ₂ NC ₂ H ₄ NH ₂	Cr	—	32	} binuclear	—
	Mo	—	32		—
	W	—	32		—
HN(CH ₂ CH ₂) ₂ NH (piperazine)	Mo	93	—	93	—
	W	93			
H ₂ NCH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂ (diethylene triamine) (dien)	Cr	—	—	32, 37, 94	—
	Mo	—	—	32, 37, 84	—
	W	—	—	32, 37	—
C ₅ H ₈ N ₂ (2-methylpyrazine)	Cr	—	95	—	—
	Mo	—	95	—	—
R ₂ NCH ₂ NR ₂ (tetraalkylmethylene diamines)	Mo	—	95	—	—
(CH ₂ NR) ₃	Mo	95	—	95	—
C ₄ H ₈ NH (pyrrolidine)	Mo	93	93	—	—
	W	93	93	—	—

O(CH ₂ CH ₂) ₂ NH (morpholine)	Cr	93	—	—	—
	Mo	93	93	93	—
	W	93	93	—	—
C ₅ H ₅ N (py)	Cr	87, 91, 32, 88, 98	32	86, 97	—
	Mo	32, 96	32, 96, 82	—	—
	W	32, 89, 82	32, 89, 82	—	—
(CH ₃) ₂ C ₅ H ₃ N (2,6-lutidine)	Cr	99	—	—	—
4-ClC ₅ H ₄ N	Cr	99	—	—	—
C ₉ H ₇ N (quinoline)	Cr	99	—	—	—
	Mo	95	—	—	—
C ₉ H ₇ N (isoquinoline)	Cr	99	—	—	—
H ₂ NC ₅ H ₄ N (4-aminopyridine)	Mo	—	90	90	—
	W	—	—	—	—
H ₂ NC ₉ H ₆ N (8-aminoquinoline)	Cr	—	95	—	—
C ₁₀ H ₈ N ₂ (2,2'-dipyridyl) (dipy)	Cr	—	32, 95, 100–103	—	—
	Mo	—	101, 32, 95, 102	—	101
	W	—	32, 82, 102, 101	—	101
C ₁₂ H ₈ N ₂ (<i>o</i> -phenanthroline) (<i>o</i> -phen)	Cr	—	101, 86	—	—
	Mo	—	—	—	101
	W	—	—	—	101

TABLE V—*continued*

Ligand	Metal	[M(CO) ₅ L]	[M(CO) ₄ L ₂]	[M(CO) ₃ L ₃]	[M(CO) ₂ L ₄]
CH ₃ CN	Cr	105, 107, 108	107, 108	106, 108	—
	Mo	107, 108	104, 107, 108	106, 107, 108	—
	W	52, 104, 107, 108	104, 107, 108, 52	106, 107, 108, 52	—
C ₆ H ₅ CN	Cr	105	—	—	—
	Mo	—	—	—	—
	W	—	—	—	—
C ₂ H ₃ CN	Cr	108	108	—	—
	Mo	108	108	108	—
	W	108, 109, 110	108, 110	108, 110	—
Dipy or <i>o</i> -phen + NH ₃	Cr	—	—	81	—
	Mo	—	—	81	—
	W	—	—	81	—
Dipy + py, P(C ₆ H ₅) ₃ , or S(C ₆ H ₅) ₂	Mo	—	—	111	—
CH ₃ NC	Cr	—	—	86, 49	—
	Mo	47	47	47, 49	—
C ₂ H ₅ NC	Mo	47	47	47	—
C ₆ H ₅ NC	Cr	—	—	86	—
	Mo	48	48	48	—
CH ₃ OC ₆ H ₄ NC	Cr	112	—	86	—
	Mo	112	—	49	—
	W	112	—	—	—

$p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$	Cr	—	—	49	—
	Mo	—	—	49	—
$\text{P}(\text{CH}_3)_3$	Mo	29, 117	29, 117	29, 117	—
$\text{P}(\text{C}_2\text{H}_5)_3$	Cr	29	29	29	—
	Mo	29, 116, 117	29, 116, 117	29, 117	117
	W	29	29, 116	29	—
$\text{P}(\text{C}_4\text{H}_9)_3$	Cr	115	—	—	—
$\text{P}(\text{C}_6\text{H}_5)_3$	Cr	114, 115	113, 115	37	—
	Mo	29, 114, 115, 117	113, 117, 29	37, 84, 117, 29	—
	W	114, 115	113	37	—
$\text{PCl}_2\text{C}_6\text{H}_5$	Mo	—	—	37	—
$\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$	Cr	114, 115	—	—	—
$\text{P}[\text{N}(\text{CH}_3)_2]_3$	Cr	71	71	—	—
	Mo	71	71	—	—
	W	—	71	—	—
PBr_2CH_3	Mo	29, 117	29, 117	29, 117	—
$\text{P}(\text{OCH}_3)_3$	Mo	29, 117	29, 117	29, 117	29
$\text{P}(\text{OC}_2\text{H}_5)_3$	Mo	29, 117	29, 117	29, 116, 117	117
$\text{P}(\text{OC}_4\text{H}_9)_3$	Cr	—	115	115	—

TABLE V—*continued*

Ligand	Metal	[M(CO) ₅ L]	[M(CO) ₄ L ₂]	[M(CO) ₃ L ₃]	[M(CO) ₂ L ₄]
P(OC ₆ H ₅) ₃	Cr	114, 115	114, 115	114, 115	—
	Mo	29, 115, 117	29, 115, 117	29, 115, 117	—
P(OCH ₂) ₃ CCH ₃	Cr	117a	117a	—	—
	Mo	117a	117a	—	—
	W	117a	117a	—	—
PCl ₂ (OC ₂ H ₅)	Mo	29, 117	29, 117	29, 117	29
PCl ₃	Cr	29	29	—	—
	Mo	29, 117	29, 117	37, 117, 29	29
	W	29	29	—	—
PF ₂ (OR) (R = C ₃ H ₇ , C ₆ H ₅)	Mo	—	—	118	—
PF(O ₂ C ₆ H ₄)	Mo	—	—	118	—
PF ₂ NR ₂ (R = CH ₃ , C ₂ H ₅ ; R ₂ = C ₅ H ₁₀)	Mo	—	—	119	119
PF ₂ CH ₂ Cl	Mo	—	—	120	—
PF ₃	Cr	—	121	121, 121a	121
	Mo	121b	121, 121b	121, 121b	121, 121b

[P(C ₆ H ₅) ₂] ₂ C ₂ H ₄ (diphosphine)	Cr	—	122, 123	123	} binuclear	122, 123
	Mo	—	122, 123	123		122, 123, 124
	W	—	122, 123	123		122, 123
[P(C ₆ H ₅) ₂] ₂ CH ₂	Cr	—	122	—		122
	Mo	—	122	—		—
	W	—	122	—		—
[P(C ₂ H ₅) ₂] ₂ C ₂ H ₄	Cr	—	122	—		122
	Mo	—	122	—		—
	W	—	122	—		—
<i>o</i> -[P(C ₂ H ₅) ₂]C ₆ H ₄	Cr	—	122	—		122
	Mo	—	122	—		122
	W	—	122	—		122
P(C ₆ H ₅)[C ₆ H ₄ P(C ₂ H ₅) ₂] ₂	Cr	—	—	122		—
	Mo	—	—	122		—
	W	—	—	122		—
CH ₃ C[CH ₂ P(C ₆ H ₅) ₂] ₃	Cr	—	—	122		—
	Mo	—	—	122		—
	W	—	—	122		—
P(C ₆ H ₅)[CH ₂ CH ₂ P(C ₆ H ₅) ₂] ₂	Cr	—	—	122		—
	Mo	—	—	122		—
	W	—	—	122		—
P ₂ (CH ₃) ₄	Cr	125 <i>a</i> , 126	} binuclear	—		—
	Mo	125, 125 <i>a</i> , 126		—		—
	W	125, 125 <i>a</i> , 126		—		—

TABLE V—*continued*

Ligand	Metal	[M(CO) ₅ L]	[M(CO) ₄ L ₂]	[M(CO) ₃ L ₃]	[M(CO) ₂ L ₄]
P ₂ (C ₂ H ₅) ₄	Mo W	125 } binuclear 125 }	—	—	—
As(C ₂ H ₅) ₃	Mo	127	127	127	—
As(C ₆ H ₅) ₃	Cr Mo W	114, 115 127 —	— 127 —	32 37, 84 37	— — —
As(C ₅ H ₁₀ N) ₃	Mo	127	127	—	—
As(OCH ₃) ₃	Mo	127	127	127	—
AsCl ₃	Cr Mo W	— 127 —	— 127 —	— 37 —	— — —
As ₂ (CH ₃) ₄	Cr Mo W	126 } binuclear 125 } 125 }	126 } polymeric 126 } —	— — —	— — —
{ <i>o</i> -[As(CH ₃) ₂] ₂ C ₆ H ₄ } (diarsine)	Cr Mo W	— — —	128, 129 128, 129 128, 129	— — —	128, 129 128, 129 128, 129
<i>o</i> -[As(C ₂ H ₅) ₂] ₂ C ₆ H ₄	Cr Mo W	— — —	— — —	— — —	37 37 37

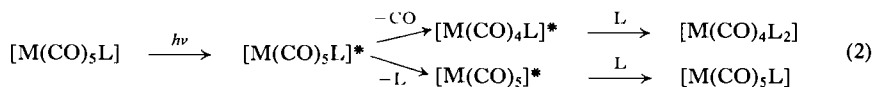
$[\text{As}(\text{C}_6\text{H}_5)_2]_2\text{C}_2\text{H}_4$	Cr	—	130	—	130
	Mo	—	130	130	130
	W	—	130	130	—
} binuclear					
$\text{CH}_3\text{C}[\text{CH}_2\text{As}(\text{CH}_3)_2]_3$	Cr	—	—	130a	—
	Mo	—	—	130a	—
	W	—	—	130a	—
$\text{Sb}(\text{C}_2\text{H}_5)_3$	Mo	46	46	46	—
$\text{Sb}(\text{C}_6\text{H}_5)_3$	Cr	114, 115	—	37	—
	Mo	46	46	37	—
	W	—	—	37	—
$\text{SbCl}(\text{C}_2\text{H}_5)_2$	Mo	46	—	—	—
$\text{SbCl}(\text{C}_2\text{H}_5)_2 + \text{Sb}(\text{C}_2\text{H}_5)_3$	Mo	—	—	46	—
SbCl_3	Mo	—	—	37	—
$\text{Bi}(\text{C}_2\text{H}_5)_3$	Mo	46	46	—	—
$\text{Bi}(\text{C}_6\text{H}_5)_3$	Mo	46	—	—	—
$(\text{CH}_3)_2\text{NCHO}$	Mo	52	—	—	—
	W	52	52	—	—
$\text{CH}_3\text{COCH}_3, (\text{C}_2\text{H}_5)_2\text{O}, \text{C}_2\text{H}_5\text{OH}$	W	52	—	—	—
$(\text{C}_3\text{H}_7)_2\text{O}, \text{CH}_3\text{NHCHO}, \text{C}_6\text{H}_{13}\text{OH}$	Mo	52	—	—	—
$(\text{CH}_3)_2\text{SO}$ or $(\text{C}_6\text{H}_5)_3\text{PO}$	Mo	—	—	84	—

TABLE V—*continued*

Ligand	Metal	[M(CO) ₅ L]	[M(CO) ₄ L ₂]	[M(CO) ₃ L ₃]	[M(CO) ₂ L ₄]
(CH ₃ OCH ₂ CH ₂) ₂ O	Mo	—	—	<i>131</i>	—
S(CH ₃) ₂	Mo	—	—	<i>44, 132</i>	—
S(C ₂ H ₅) ₂	Mo	<i>127</i>	<i>127</i>	<i>44, 127</i>	—
S(CH ₂) ₄	Mo	—	—	<i>44, 132</i>	—
SC(NH ₂) ₂	Mo	—	—	<i>44</i>	—
CH ₃ SCH ₂ CH ₂ SCH ₃	Cr	—	<i>45</i>	—	—
	Mo	—	<i>45</i>	—	—
	W	—	<i>45</i>	—	—
(CH ₃ CH ₂ SCH ₂ CH ₂) ₂ S	Cr	—	<i>45</i>	—	—
	Mo	—	<i>45</i>	—	—

^a Italic numbers are references.

pounds (133, 137), but less than one for the preparation of the disubstituted materials (137, 139). The excited $[M(CO)_5L]$ molecule can lose either a carbonyl group or the molecule L, only the first mode of reaction then leading to the disubstituted species [Eq. (2)] (137, 139).



The carbon monoxide present in the solution may also react with the products or the coordinatively unsaturated species, effectively reversing the reaction (137, 138). The differences in the behavior of the three carbonyls and the effect of solvent have been noted, so that one may choose the proper conditions for obtaining the desired product (137, 138, 139). For hexacarbonylchromium and -tungsten, the order of reactivity of donors is pyridine > tetrahydrofuran > triethylamine > acetonitrile > 1,3-cyclohexadiene > ethyl acetate > acetone > toluene. In the case of hexacarbonylmolybdenum, acetonitrile and toluene are advanced in the series (138). Other workers have studied the photochemical reaction of $[Mo(CO)_6]$ with nitriles (107). The infrared spectrum of irradiated hexacarbonylmetal glasses at $-180^\circ C$ indicates the presence of the C_{4v} (tetragonal pyramidal) $[M(CO)_5]$ species; in the case of molybdenum, this rearranges at $-155^\circ C$ to the D_{3h} (trigonal bipyramidal) structure (140).

Great use has been made of infrared spectra (28, 29, 31, 32, 33, 46, 47, 48, 52, 107, 108, 116, 117, 127) in assigning configurations to the Group VI metal complexes, as indicated in Section II, C. The vibrations of bonds within the donor molecules have been used to deduce their mode of attachment. A lowering of the NH frequency in morpholine complexes, compared to that of the free ligand, has been cited as evidence for bonding to the metal through nitrogen rather than oxygen (93). The shift to higher frequency of the CN vibration in the infrared spectra of nitrile derivatives has been taken to show nitrogen-metal bonding (52, 108, 109, 110). Nuclear magnetic resonance data are in agreement with this conclusion (108, 110). Interestingly, although the mono- and disubstituted acrylonitrile derivatives of the hexacarbonyls appear to have nitrogen-metal bonds (108, 109, 110), tricarbonyltris(acrylonitrile)tungsten and -molybdenum appear to have olefin-metal bonding instead (108, 110).

A few general comments on the nature of the $[M(CO)_{6-n}L_n]$ complexes are in order; most demonstrate the principles cited in Section II. Bonding

through phosphorus and arsenic generally confers greater stability than does bonding through nitrogen or oxygen. It becomes increasingly difficult to displace additional carbonyl groups as the degree of substitution increases. Most of the $[\text{M}(\text{CO})_4\text{L}_2]$ and $[\text{M}(\text{CO})_3\text{L}_3]$ complexes are found in the *cis* form, although the *trans* form has been isolated in a few cases (108, 110, 116, 117, 122). *Cis-trans* isomerization in solution has been noted (122), as has disproportionation of $[\text{M}(\text{CO})_5\text{L}]$ or $[\text{M}(\text{CO})_3\text{L}_3]$ to $[\text{M}(\text{CO})_4\text{L}_2]$ species (115).

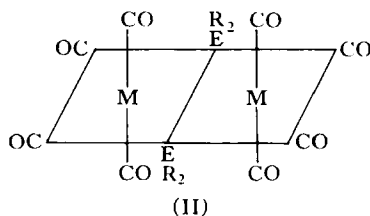
Chelating ligands normally react with the Group VI carbonyls to give more ready substitution to a greater degree and more stable derivatives than do their monodentate analogs. The first such ligand to gain prominence was Nyholm's "diarsine" [*o*-phenylenebis(dimethylarsine)] (128, 129). Also studied have been di- and tri(tertiary phosphine) (122, 123) and di- and tri(tertiary arsine) donors (130, 130a). The chelating bases have given numerous $[\text{M}(\text{CO})_2\text{L}_4]$ species, whereas with only a few monodentate ligands, e.g., $\text{P}(\text{OC}_2\text{H}_5)_3$, can one go past the trisubstituted compounds. Tris(dimethylamino)phosphine, even in reactions with tricarbonyl(cycloheptatrienyl)metal complexes, gives only the products $[\text{M}(\text{CO})_4\text{L}_2]$ (71). Also worthy of note are the bridged species $[\text{M}_2(\text{CO})_6\text{L}_3]$, formed with both 1,2-bis(diphenylphosphino)ethane and its arsenic analog (123, 130).

The reaction of 2,2'-dipyridyl with the metal hexacarbonyls normally produces only the tetracarbonyl(dipyridyl) derivatives (102). The subsequent reaction of these complexes with monodentate ligands gives tricarbonyl(ligand)(dipyridyl) complexes, in which a carbonyl group *cis* to the dipyridyl has been replaced. It has been suggested that the known difficulty of replacing carbonyls *trans* to a less strongly π -bonding group makes preparation of dicarbonylbis(dipyridyl)metal compounds impossible (111). However, under very drastic conditions it is possible to replace four carbonyl groups with two molecules of dipyridyl (101). In the case of chromium, the dicarbonyl compound then disproportionates to tris(dipyridyl)chromium and the tetracarbonyl(dipyridyl) compound (101).

The use of liquid ammonia well above its normal boiling point as a solvent and reactant has been fruitful. The metal hexacarbonyls themselves have afforded the complexes $[\text{M}(\text{CO})_3(\text{NH}_3)_3]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $[\text{Cr}(\text{CO})_5\text{NH}_3]$ (81). The tetracarbonyl(dipyridyl)metal complexes of chromium, molybdenum, and tungsten and their (*o*-phen) analogs react with liquid ammonia to give very air-sensitive compounds, such as $[\text{M}(\text{CO})_3(\text{dipy})(\text{NH}_3)]$, which finally yield mainly $[\text{M}(\text{CO})_3(\text{NH}_3)_3]$ (81). The $[\text{M}(\text{CO})_4$

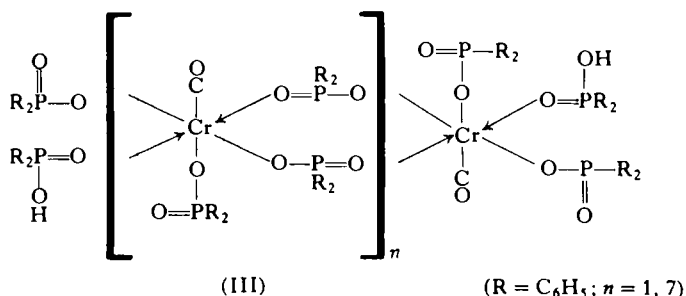
(dipy)] species react with potassium cyanide in liquid ammonia to give the $[\text{Cr}(\text{CN})_2(\text{CO})_4]^{2-}$ and $[\text{M}(\text{CN})_3(\text{CO})_3]^{3-}$ ($\text{M} = \text{Mo}, \text{W}$) anions (81).

An interesting group of complexes is formed by treatment of the metal carbonyl with biphosphines or biarsines of the form R_2EER_2 with $\text{E} = \text{P}, \text{As}$; and $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$ (125, 126). At $180^\circ\text{--}200^\circ\text{C}$ one obtains compounds of the type $[(\text{CO})_5\text{MR}_2\text{EER}_2\text{M}(\text{CO})_5]$, which are analogous to the simple $[\text{M}(\text{CO})_5\text{L}]$ compounds. This type is known for chromium [$\text{ER}_2 = \text{P}(\text{CH}_3)_2$ (125a, 126), $\text{As}(\text{CH}_3)_2$ (126)], molybdenum [$\text{ER}_2 = \text{P}(\text{CH}_3)_2$ (125, 125a, 126), $\text{P}(\text{C}_2\text{H}_5)_2$ (125), $\text{As}(\text{CH}_3)_2$ (125, 126)], and tungsten [$\text{ER}_2 = \text{P}(\text{CH}_3)_2$ (125, 125a, 126), $\text{P}(\text{C}_2\text{H}_5)_2$ (125), $\text{As}(\text{CH}_3)_2$ (125, 126)]. From tetramethylbiarsine a class of polymers of formula $[\text{M}(\text{CO})_4\text{As}_2(\text{CH}_3)_4]_n$ is also obtained ($\text{M} = \text{Cr}, n = 13$; $\text{M} = \text{Mo}, n = 20$) (126). On the other hand, at higher temperatures, after longer times, the $\text{E}\text{--}\text{E}$ bond is cleaved, and the consequent derivatives of composition $[\text{M}(\text{CO})_4\text{ER}_2]_2$ contain --ER_2 functioning as a three-electron bridging group. In the resulting structure (II), which may be slightly folded on the $\text{E}\text{--}\text{E}$ line, a metal-metal



bond is postulated to explain the observed diamagnetism (125). This type of complex is known for chromium [$\text{ER}_2 = \text{P}(\text{CH}_3)_2$ (125, 125a, 126), $\text{P}(\text{C}_2\text{H}_5)_2$ (125)], molybdenum [$\text{ER}_2 = \text{P}(\text{CH}_3)_2$ (126, 125a), $\text{P}(\text{C}_2\text{H}_5)_2$ (125), $\text{As}(\text{CH}_3)_2$ (125, 126), $\text{As}(\text{C}_6\text{H}_5)_2$ (125)], and tungsten [$\text{ER}_2 = \text{P}(\text{CH}_3)_2$ (125, 125a, 126), $\text{P}(\text{C}_2\text{H}_5)_2$ (125), $\text{As}(\text{CH}_3)_2$ (125, 126)].

A few derivatives are known in which the Group VI metal has been oxidized by an oxygen-containing ligand. Treatment of hexacarbonylmolybdenum with sulfur trioxide in liquid sulfur dioxide forms pyrosulfato(tetracarbonyl)molybdenum, $\{\text{Mo}[\text{O}(\text{SO}_3)_2](\text{CO})_4\}$, as an air-stable, hygroscopic molybdenum(II) compound, which may be polymeric (141). Treatment of hexacarbonylchromium with diphenylphosphinic acid yields a number of species of varying molecular weight, formulated as (III) (142).

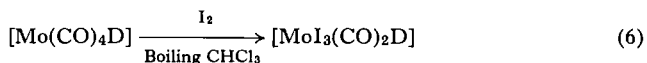
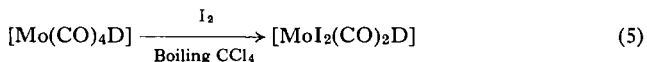
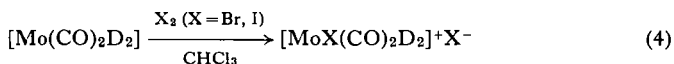
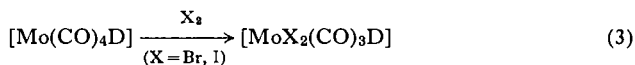


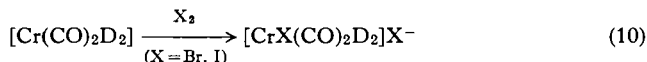
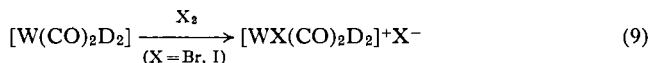
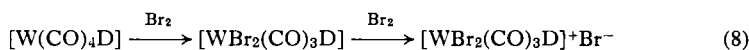
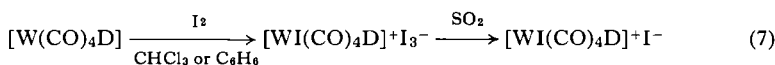
2. Indirect Methods of Synthesis

The oxidation by water of the Group VI carbonylmetallate ions in the presence of cyanide ion has been shown to give complex ions containing chromium(0), e.g., $[\text{MCN}(\text{CO})_5]^-$ and $[\text{M}(\text{CN})_2(\text{CO})_4]^{2-}$ (82, 103). When the carbonylmetallate ions are thus oxidized in the presence of bases, substituted carbonyls of the zero-valent metal are formed. Complexes prepared in this way include $[\text{M}(\text{CO})_5\text{NH}_3]$, M = Mo, W (82); $[\text{M}(\text{CO})_3(\text{NH}_3)_3]$, M = Cr (83, 86), Mo (82, 84), W (82, 85); $[\text{Mo}(\text{CO})_3(\text{dien})]$ (84); $[\text{M}(\text{CO})_3(\text{en})_3\text{M}(\text{CO})_3]$, M = Cr (83), Mo (84); $[\text{M}(\text{CO})_5(\text{RNH}_2)]$, M = Cr (87, 91), Mo (91), W (82); $[\text{M}(\text{CO})_5(\text{py})]$, M = Cr (100), W (82); $[\text{M}(\text{CO})_4(\text{py})_2]$, M = Mo (82), W (82); $[\text{M}(\text{CO})_4(\text{dipy})]$, M = Cr (100, 103), W (82).

3. Halogenation of the Simple Complexes

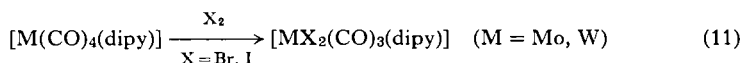
Besides ligand exchange and further substitution (not to mention decomposition), few reactions have been noted for these complexes. One interesting example is halogenation, first studied by Nyholm in the case of diarsine complexes (143, 144). The products are sometimes novel seven-coordinate species, depending on conditions [Eqs. (3–10), diarsine = D] (143, 144). The tendency to lose carbon monoxide in these reactions





decreases in the order $\text{Cr} > \text{Mo} > \text{W}$. Thus, treatment of tetracarbonyl-(diarsine)chromium with halogen leads only to decomposition (144). However, careful halogenation of dicarbonylbis(diarsine)chromium leads to mixed-seven-coordinate complexes like those of molybdenum and tungsten (144a).

The same type of behavior has also been noted for the dipyridyl complexes. Again, $[\text{Cr}(\text{CO})_4(\text{dipy})]$ yields no isolable products on treatment with halogen, but the molybdenum and tungsten compounds do [Eq. (11)] (102).



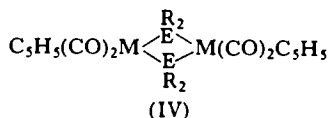
Similarly, iodination of tetracarbonyl(2,5-dithiahexane)metal (Cr , Mo , W) complexes gives isolable seven-coordinate products $[\text{MI}_2(\text{CO})_3(2,5\text{-dithiahexane})]$ only for molybdenum and tungsten. Reduction of these iodo compounds with lithium aluminum hydride forms unisolable materials with M-H bonds (45).

4. Derivatives of Organometal Carbonyls

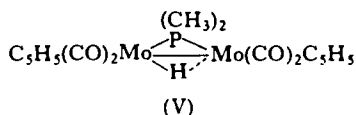
The treatment of tricarbonyl(cycloheptatriene) or (arene) metal complexes with donors has been cited as a good route to the $[\text{M}(\text{CO})_3\text{L}_3]$ compounds (37, 114, 115). When initiated by ultraviolet light this reaction may be controlled to give dicarbonyl(arene)(donor) metal complexes (145, 146, 146a). The nature of the group X as well as the donor L influences the stability of the products of the type $[\text{Cr}(\text{CO})_2(\text{L})(\text{X}-\text{C}_6\text{H}_4)]$. Electron-withdrawing X groups favor donation of electrons, $\text{L} \rightarrow \text{Cr}$, but electron-releasing groups favor back-bonding $\text{Cr} \rightarrow \text{L}$. For maximum stability then, X and L must complement each other's electron-donating and electron-accepting tendencies. For example, with a poor π -acceptor ligand such as acetonitrile, terephthalic acid forms a more stable mixed complex than does

mesitylene (146). The sigma component of the Cr—L bond is the main determinant of stability of that bond (146a).

Hayter's detailed and comprehensive work on tetrasubstituted biarsine or biphosphine ligands has been extended to reactions with the hexacarbonyldicyclopentadienyldimetal compounds, $[\text{M}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$). The most characteristic products are dimers (without metal-metal



bonds) (IV) (70). One of the same products is obtained by treatment of $\text{AsCl}(\text{CH}_3)_2$ with $\text{Na}^+[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]^-$. However, treatment of this sodium salt with $\text{PCl}(\text{CH}_3)_2$ gives a peculiar hydride (V). The unexpected



product from the reaction between $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ and $\text{P}_2(\text{C}_6\text{H}_5)_4$ is a trimer, $[\text{Mo}(\text{C}_5\text{H}_5)\text{P}(\text{C}_6\text{H}_5)_2(\text{CO})]_3$, with phosphorus, but not carbonyl, bridges (70).

When $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ is treated with $\text{As}_2(\text{CF}_3)_4$, the product is a monomeric species, $[\text{Mo}(\text{C}_5\text{H}_5)\text{As}(\text{CF}_3)_2(\text{CO})_3]$, which is converted by irradiation into the arsenic-bridged species $[\text{Mo}(\text{C}_5\text{H}_5)\text{As}(\text{CF}_3)_2(\text{CO})_2]_2$ (147). Although all the carbon monoxide is lost when $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ is treated with dimethyldisulfide (148), the reaction between $[\text{MoH}(\text{C}_5\text{H}_5)(\text{CO})_3]$ and dimethyl disulfide gives a dimeric complex, $[\text{Mo}(\text{C}_5\text{H}_5)\text{SCH}_3(\text{CO})_2]_2$ (149). The tungsten analog is similarly made (149). The correspondence between —SR and —PR₂ bridging groups is clearly seen here, although in this case the sulfur-containing species apparently exists in geometrical isomers (149), whereas the phosphorus-containing species does not (70).

Substitutions have also been carried out upon the cyclopentadienyl-molybdenum carbonyl halides. Although treatment of $[\text{MoCl}(\text{C}_5\text{H}_5)(\text{CO})_3]$ with phenyl isocyanide gives no carbonyl-containing product, from

$[\text{MoI}(\text{C}_5\text{H}_5)(\text{CO})_3]$ and phenyl isocyanide one may prepare the complex $[\text{MoI}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{CNC}_6\text{H}_5)]$ (150). Related complexes $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{CNCH}_3)_2]^+\text{I}^-$, and $[\text{W}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{CNCH}_3)]^+\text{I}^-$ are obtained by alkylation of the appropriate complex cyanides (151). The reactions between $[\text{MoI}(\text{C}_5\text{H}_5)(\text{CO})_3]$ or $[\text{MoI}(\text{C}_7\text{H}_7)(\text{CO})_2]$ and tris(dimethylamino)phosphine (tdp) give, respectively, two isomers of composition $[\text{MoI}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{tdp})]$, and a single form of $[\text{MoI}(\text{C}_7\text{H}_7)(\text{CO})(\text{tdp})]$ (71). If the alkylmolybdenum compound $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CH}_2\text{SCH}_3)(\text{CO})_3]$ is heated or irradiated, one may isolate a compound $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CH}_2\text{SCH}_3)(\text{CO})_2]$ of perhaps novel structure (152).

The metathetical reaction between $[\text{CH}_3\text{OC}_6\text{H}_4\text{N}_2][\text{BF}_4]$ and $\text{Na}[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]$ gives a material $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{CH}_3\text{OC}_6\text{H}_4\text{N}_2)]$ in which the diazonium group acts as a novel three-electron donor (152a).

D. Manganese and Rhenium

1. Manganese

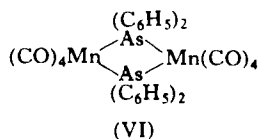
a. *The Direct Reaction of the Carbonyl with Bases.* The base-substituted carbonyls of the Group VII elements are more varied in nature than those of the Group VI metals. This fact stems from the number of different ways in which the zero-valent atoms can obtain the 11 electrons needed to satisfy the rare-gas rule. The need for an odd number of electrons is met if one ligand is a cyclopentadienyl, alkyl, acyl, halide, or nitrosyl group, or if the species considered is a mono-anion or cation, or if a metal-metal bond is present.

The reasons why different types of donors produce substitution or disproportionation of manganese carbonyl have been discussed and correlations have been drawn with these tendencies in other metal carbonyls (153). Although most strong nitrogen bases with little π -acceptor tendency, including pyridine, cause disproportionation of decacarbonyldimanganese to give compounds containing the pentacarbonylmanganate(-1) ion, aniline and *o*-phenylenediamine give monosubstituted derivatives $[\text{Mn}(\text{CO})_4\text{L}]$ (153). On the other hand, nitrogen donors with substantial π -acceptor properties furnish the unsymmetrical products $[(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_3\text{L}_2]$ ($\text{L}_2 = \text{dipyridyl}$, *o*-phenanthroline) (153, 154). The dipyridyl complex may also be obtained from $[\text{Mn}_2\text{H}_2(\text{CO})_9]$ and the ligand (153). Oxidation of the $[\text{Mn}_2\text{H}(\text{CO})_9]^-$ anion with hydroxylamine sulfonic acid forms an ammonia complex, $[\text{Mn}_2(\text{CO})_9(\text{NH}_3)]$ (155). Irradiation of the

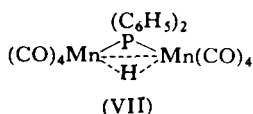
$[\text{Mn}_2(\text{CO})_8\text{L}_2]$ species gives $[\text{Mn}_2(\text{CO})_{10}]$ and the dimers $[\text{Mn}(\text{CO})_3\text{L}_2]_2$ (153, 154).

The heating of decacarbonyldimanganese with phosphorus, arsenic, or antimony bases provides the paramagnetic monomers $[\text{Mn}(\text{CO})_4\text{L}]$, where $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (15, 156), $\text{P}(\text{C}_2\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, and $\text{Sb}(\text{C}_6\text{H}_5)_3$ (15) or the diamagnetic dimers $[\text{Mn}(\text{CO})_4\text{L}]_2$, $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$ and $\text{P}(\text{OC}_6\text{H}_5)_3$ (15). The monomers have trigonal bipyramidal configurations, and the dimeric species, which dissociate in solution at 100°C , are held together by metal-metal bonds only, since bridging carbonyl groups are lacking (15). Under the influence of ultraviolet light in cyclohexane solution, the direct reaction yields the dimers for $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_4\text{F})_3$, and $\text{As}(\text{C}_6\text{H}_5)_3$, although triphenylarsine affords evidence of some monomer formation (12, 157). With *o*-phenylenebis(dimethylarsine), the direct reaction gives both the monomer and the dimer of stoichiometry $[\text{Mn}(\text{CO})_3(\text{diarsine})]$. The latter compound dissociates irreversibly upon heating (158). The chelating ligand 1,2-bis(diphenylphosphino)ethane has been reported to react with $[\text{Mn}_2(\text{CO})_{10}]$, forming, depending on conditions, $[\text{Mn}_2(\text{CO})_8(\text{diphosphine})]$ (17), paramagnetic $[\text{Mn}(\text{CO})_3(\text{diphosphine})]$, paramagnetic $[\text{Mn}(\text{CO})(\text{diphosphine})_2]$, or ionic $[\text{Mn}(\text{CO})_2(\text{diphosphine})_2]^+ [\text{Mn}(\text{CO})_5]^-$ (159).

Under very drastic conditions, treatment of $[\text{Mn}_2(\text{CO})_{10}]$ with triphenylarsine produces a dimeric arsenic-bridged compound, $[\text{MnAs}(\text{C}_6\text{H}_5)_2(\text{CO})_4]_2$, (VI), in which the $\text{As}(\text{C}_6\text{H}_5)_2$ group is a three-electron donor



(157, 160). This compound may also be prepared by the reaction between diphenylarsine, chloropentacarbonylmanganese, and *p*-toluidine (161). Direct reaction between $[\text{Mn}_2(\text{CO})_{10}]$ and $\text{As}_2(\text{CH}_3)_4$ gives the analogous $[\text{MnAs}(\text{CH}_3)_2(\text{CO})_4]_2$ (162). The corresponding product is obtained with $\text{As}_2(\text{CF}_3)_4$ as reactant (147). A phosphorus analog, $[\text{MnP}(\text{C}_6\text{H}_5)_2(\text{CO})_4]_2$ may be obtained by reaction of $\text{PCl}(\text{C}_6\text{H}_5)_2$ and $\text{Na}[\text{Mn}(\text{CO})_5]$ in tetrahydrofuran (161, 162) or by direct combination of $[\text{Mn}_2(\text{CO})_{10}]$ and $\text{P}_2(\text{C}_6\text{H}_5)_4$ (161). A by-product of the latter process is an unusual, diamagnetic hydride complex (VII), which is also accessible by treatment of



$[\text{MnP}(\text{C}_6\text{H}_5)_2(\text{CO})_4]_2$ with triphenylphosphine and *p*-toluidine (162). The condensation of $\text{Na}[\text{Mn}(\text{CO})_5]$ with $\text{PCl}(\text{CH}_3)_2$ produces initially a singly-bridged binuclear complex $[(\text{CO})_5\text{Mn}-\text{P}(\text{CH}_3)_2-\text{Mn}(\text{CO})_4\text{P}(\text{CH}_3)_2]$, which on boiling in toluene yields the doubly-bridged $[\text{MnP}(\text{CH}_3)_2(\text{CO})_4]_2$ (161, 163). The reaction between $[\text{Mn}_2(\text{CO})_{10}]$ and $(\text{CF}_3)_2\text{PI}$ gives a compound of composition $\{\text{Mn}_2\text{I}[\text{P}(\text{CF}_3)_2](\text{CO})_8\}$, probably of a structure similar to (VI), with phosphorus and iodine bridges (164, 164a). When treated with the unusual ligand, diphenyltellurium, decacarbonyldimanganese yields the tellurium-bridged species $[\text{Mn}(\text{TeC}_6\text{H}_5)(\text{CO})_4]_2$ analogous to the arsenic and phosphorus-bridged compounds cited above (165).

Sulfur-bridged carbonylmanganese complexes of formula $[\text{MnSR}(\text{CO})_4]_2$, with $\text{R} = \text{CH}_3$, C_2H_5 , and C_4H_9 are prepared in high yields by treatment of $[\text{Mn}(\text{CO})_5\text{H}]$ with the dialkyl disulfides RSSR (149); $[\text{Mn}(\text{SC}_6\text{H}_5)(\text{CO})_4]_2$ is obtained quantitatively from $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $\text{C}_6\text{H}_5\text{SH}$ (166). Materials of similar composition $[\text{MnSR}(\text{CO})_3]_{2\text{ or }3}$, $\text{R} = \text{C}_2\text{H}_5$, C_3H_7 , C_4H_9 , C_6H_5 , $\text{CH}_3\text{C}_6\text{H}_4$, $\text{C}_6\text{H}_5\text{CH}_2$ (possibly identical with the $[\text{MnSR}(\text{CO})_4]_2$ species) were prepared by irradiation of mixtures of $[\text{Mn}_2(\text{CO})_{10}]$ or $[\text{MnCl}(\text{CO})_5]$, with the appropriate mercaptans (167).

Like the simple carbonyl, the phosphine-substituted manganese carbonyls are readily reduced by sodium amalgam in tetrahydrofuran (168, 169). The resulting anions $[\text{Mn}(\text{CO})_4\text{PR}_3]^-$ undergo reactions expected by analogy with the behavior of $[\text{Mn}(\text{CO})_5]^-$, giving mercury salts, alkyls, acyls, and hydrides when treated with mercuric cyanide, alkyl iodides, acid chlorides or anhydrides, or acids, respectively (168, 169). The hydride $[\text{MnH}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ ("pseudo- $[\text{Fe}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ ") is not at all acidic, whereas $[\text{MnH}(\text{CO})_5]$ itself is only slightly acidic (169).

Complexes containing bidentate sulfur-bonded ligands which form four-membered rings with the manganese atom are obtained by the reaction between $[\text{MnBr}(\text{CO})_5]$ and dithiobenzoic acid (169a) or sodium *N,N*-dialkyl-dithiocarbamates (169b); the products have the compositions $[\text{Mn}(\text{S}_2\text{CC}_6\text{H}_5)(\text{CO})_4]$ or $[\text{Mn}(\text{S}_2\text{CNR}_2)(\text{CO})_4]$ ($\text{R} = \text{CH}_3$, C_2H_5) respectively.

b. *Nitrosyl-Carbonyl Derivatives*. Eleven electrons may be donated by a combination of three nitrosyl groups and one carbonyl group, or of one

nitrosyl group and four carbonyl groups. In the case of manganese both possibilities have been realized with the synthesis from iodopentacarbonylmanganese and nitric oxide of $[\text{MnCO}(\text{NO})_3]$ ("pseudonickel tetracarbonyl") (18, 170), and the synthesis from hydridopentacarbonylmanganese and *N*-nitroso-*N*-methyl-*p*-toluenesulfonamide of $[\text{Mn}(\text{CO})_4\text{NO}]$ ("pseudoiron pentacarbonyl"). Irradiation of the latter gives $[\text{Mn}_2(\text{CO})_7(\text{NO})_2]$ (171).

When carbonylnitrosyl metal compounds are treated with other donors, the usual result is displacement of carbonyl groups only. Thus, treatment of $[\text{MnCO}(\text{NO})_3]$ with triphenylphosphine gives only $[\text{Mn}(\text{NO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ (18). However, mixed nitrosyl(carbonyl)(donor)manganese compounds have been obtained. It was first reported that the reaction between nitric oxide and $[\text{MnI}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ or $[\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ forms only $[\text{Mn}(\text{NO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ (172), but under other conditions these reagents give, in addition, the partially substituted product $[\text{Mn}(\text{CO})_3(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]$ (173, 174). In the reaction between nitric oxide and the $[\text{Mn}(\text{CO})_4\text{L}]$ species good yields of partially substituted product $[\text{Mn}(\text{CO})_3(\text{NO})\text{L}]$ are not obtained. A better way of obtaining these compounds is to use amyl nitrite in place of nitric oxide; this has been demonstrated for $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ and $\text{P}(\text{C}_6\text{H}_{11})_3$. The dipole moment and the infrared spectrum of $[\text{Mn}(\text{CO})_3(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]$ indicate either a *cis* or *trans* trigonal bipyramidal structure. Since the dipole moment contributions of NO and CO are very similar, but the moment of $[\text{Mn}(\text{CO})_3(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]$ is much higher than that of $[\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$, it has been suggested that in the nitrosyl derivative more effective positive charge is left on the phosphorus atom than in the other case. The compound $[\text{Mn}(\text{CO})_3(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]$ reacts with excess $\text{P}(\text{C}_6\text{H}_5)_3$ or $\text{P}(\text{C}_6\text{H}_{11})_3$ at higher temperatures to give $[\text{Mn}(\text{CO})_2(\text{NO})\text{L}_2]$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, believed to have the phosphine groups in *trans* positions on the trigonal bipyramid (174).

c. *Halogenation of the Base-Carbonyl Complexes.* The base-carbonyl complexes of zero-valent manganese are easily oxidized by mild halogenating agents, as might be expected, since this might facilitate the attainment of the rare-gas configuration. Thus, $[\text{MnH}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ (169) and $[\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ (157, 169) react with carbon tetrachloride or chloroform, yielding $[\text{MnCl}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$. The halogens themselves give the analogous products (169). Irradiation in chlorinated solvents converts the complex $[\text{Mn}_2(\text{CO})_8(o\text{-phen})]$ to a mixture of $[\text{MnCl}(\text{CO})_3(o\text{-phen})]$ and $[\text{MnCl}(\text{CO})_5]$ (154). Bromination of $[\text{Mn}(\text{CO})_3(\text{diphosphine})]$ produces

$[\text{MnBr}(\text{CO})_3(\text{diphosphine})]$ (160). With $[\text{Mn}(\text{CO})_3(\text{diarsine})]_n$ ($n = 1, 2$) iodine gives $[\text{MnI}(\text{CO})_3(\text{diarsine})]$, but bromine yields an unusual paramagnetic species $[\text{MnBr}_2(\text{CO})_2(\text{diarsine})]$ (158). Oxidation of $[\text{Mn}(\text{CO})_3(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]$ with iodine, bromine, or cyanogen bromide causes loss of CO and rearrangement to form $\{\text{MnX}(\text{NO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, $\text{X} = \text{I}, \text{Br}, \text{CN}$ (174). From infrared spectra it has been concluded that the species $[\text{Mn}(\text{CO})_4\text{PR}_3]$, $[\text{Mn}(\text{CO})_4(\text{PR}_3)]^-$, and $[\text{MnH}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ all have the trigonal bipyramidal structure, while the species $[\text{MnX}(\text{CO})_4(\text{PR}_3)]$ ($\text{X} = \text{halogen}$) and $[\text{MnCH}_3(\text{CO})_4\text{PR}_3]$ probably have *cis* octahedral structures (169).

d. *Reactions of the Carbonyl Halides.* When the manganese carbonyl halides of composition $[\text{MnX}(\text{CO})_5]$ or $[\text{MnX}(\text{CO})_4]_2$ are heated with two moles of suitable base, they form disubstituted compounds of composition $[\text{MnX}(\text{CO})_3\text{L}_2]$, with $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{NH}_3$ (175), $\text{C}_6\text{H}_5\text{NH}_2$ (166), *py* (166, 176), *RNC* (166), $\text{P}(\text{C}_6\text{H}_5)_3$ (166, 176), $\text{As}(\text{C}_6\text{H}_5)_3$ (166, 176), $\text{Sb}(\text{C}_6\text{H}_5)_3$ (166), *pyridine-2-alimine* (166), $\text{Te}(\text{C}_6\text{H}_5)_2$ (165); and $\text{X} = \text{C}(\text{CN})_3$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$ (177). With chelating ligands the products are again of the type $[\text{MnX}(\text{CO})_3\text{L}_2]$, $\text{L}_2 = \text{dipy}$ (166, 176), *o*-phen (166), 2,5-dithiahexane (45), 3,6,9-trithiaundecane (45), dien (from $[\text{Mn}(\text{CO})_3(\text{mesitylene})]\text{I}$) (37), 1,2-bis(diphenylphosphino)ethane (159, 178), 1,2-bis(phenylthio)ethane (178), *o*-phenylenebis(dimethylarsine) (178). The three carbonyl groups in this type of product are mutually *cis* in most cases (165, 176). In a slightly different manner, the pentacarbonyl halides react with liquid ammonia or ethylenediamine (*en*) and dimethyl sulfoxide (*DMSO*) to give ionic complexes of the type $[\text{Mn}(\text{CO})_4\text{L}_2]^+\text{X}^-$, with $\text{L} = \text{NH}_3$, *en*, *DMSO* (166).

An interesting set of reactions is that between $[\text{MnSCN}(\text{CO})_5]$ and various bases to give complexes $[\text{MnSCN}(\text{CO})_3\text{L}_2]$. In the products when $\text{L} = \text{pyridine}$, *dipyridyl*, or *p*-toluidine, the *L* and *NCS* groups are mutually *cis*. The thiocyanate group, bonded to manganese through the *sulfur* atom in the starting material, is bonded through the *nitrogen* atom in the products. Triphenylphosphine yields a complex with N-bonded thiocyanate but *trans*-phosphine groups, and triphenylstibine yields a material with all *cis* substitution, but S-bonded thiocyanate (179). Steric conditions may be the predominant reasons for these structural differences.

The disubstituted carbonyl halides $[\text{MnX}(\text{CO})_3\text{L}_2]$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, are readily reduced by sodium amalgam to the disubstituted anions $[\text{Mn}(\text{CO})_3\text{L}_2]^-$ which undergo alkylation and other

reactions typical of the $[\text{Mn}(\text{CO})_5]^-$ anion itself. A notable product is the very stable, barely acidic hydride $\{\text{MnH}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (179a).

Detailed examination of the reaction of bromomanganese pentacarbonyl with phenyl isocyanide has shown strikingly the dependence of the extent of such reactions on solvent. In ethanol at 60° C the product is $[\text{MnBr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_2]$; in diglyme at 100° C, $[\text{MnBr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_3]$; in refluxing tetrahydrofuran, $[\text{MnBrCO}(\text{CNC}_6\text{H}_5)_4]$ as well as $[\text{MnBr}(\text{CNC}_6\text{H}_5)_5]$. The last member of this series of mixed derivatives, $[\text{MnBr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_5]$, is obtained at room temperature in tetrahydrofuran from $[\text{MnBr}(\text{CO})_4]_2$. The order of reactivity of the pentacarbonyl halides is $\text{Cl} > \text{Br} > \text{I}$ (150).

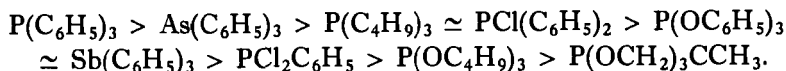
Cationic manganese(carbonyl)(phosphine) species have been produced by treatment of the dry complexes $[\text{MnCl}(\text{CO})_4\text{L}]$ or $[\text{MnCl}(\text{CO})_3\text{L}_2]$ with aluminum chloride, ferric chloride, or zinc chloride and carbon monoxide at high temperatures and pressures. Typical anions are $[\text{AlCl}_4]^-$ and $[\text{FeCl}_4]^-$. The substituted cations are easier to prepare in these systems than is $[\text{Mn}(\text{CO})_6]^+$. Obtained have been the cations $[\text{Mn}(\text{CO})_5\text{L}]^+$ and $[\text{Mn}(\text{CO})_4\text{L}_2]^+$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$ (180, 181). In the disubstituted cations the phosphines are in *trans* positions (180). The analogous ion $[\text{Mn}(\text{CO})_4(o\text{-phen})]^+$ has been obtained by similar treatment of $[\text{MnCl}(\text{CO})_3(o\text{-phen})]$ in the presence of ZnCl_2 (181). The treatment of $\{\text{MnCl}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ with benzene, triphenylphosphine, and aluminum chloride but without excess carbon monoxide gives only $\{\text{Mn}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+$ ion (by CO redistribution), as does bubbling carbon monoxide through a mixture of $\{\text{MnCl}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, benzene, and aluminum chloride (181). This pressureless synthesis has also allowed the preparation of other ions $[\text{Mn}(\text{CO})_4\text{L}_2]^+$, $\text{L} = \text{P}(\text{OC}_6\text{H}_5)_3$, $\text{Te}(\text{C}_6\text{H}_5)_2$ (181). The cation $\{\text{Mn}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+$ has also been obtained by displacement of ethylene and carbon monoxide from the cation $[\text{Mn}(\text{CO})_5(\text{CH}_2=\text{CH}_2)]^+$ (177, 182). Alkoxides combine with the disubstituted cations, forming species of the type $[\text{Mn}(\text{COOR})(\text{CO})_3\text{L}_2]$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$; $\text{R} = \text{CH}_3$, C_2H_5 , C_5H_{11} , $\text{C}_6\text{H}_5\text{CH}_2$, which still have the phosphine groups in the *trans* position. The carboalkoxy derivatives are cleaved by HX to give $[\text{Mn}(\text{CO})_4\text{L}_2]^+\text{X}^-$ (183). These halides react with sodium carbonylmetallates to give ionic complexes with carbonyl-containing cations and anions, e.g., $\{\text{Mn}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+[\text{Fe}(\text{CO})_3\text{NO}]^-$. In some cases a redox reaction converts the initially formed mixed-metal salt to a mixed-metal carbonyl. Thus, the final product from the combination of $[\text{Mn}(\text{CO})_4(o\text{-phen})]^+$ and $[\text{Co}(\text{CO})_4]^-$ is $[(\text{CO})_3(o\text{-phen})\text{MnCo}(\text{CO})_4]$. In still other

cases a ligand in the anion is exchanged for carbon monoxide; the combination of $[\text{Mn}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3]^+$ and $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]^-$ produces $[\text{Mn}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3]^+[\text{Co}(\text{CO})_4]^-$ (183a).

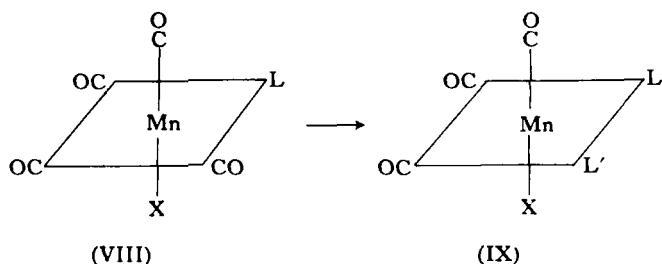
It has been shown that the reaction between nitric oxide and the substituted halides $[\text{MnX}(\text{CO})_4\text{L}]$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}$, and $\text{L} = \text{PR}_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{Sb}(\text{C}_6\text{H}_5)_3, \text{py}$ gives complete loss of carbon monoxide, with the formation of the corresponding $[\text{Mn}(\text{NO})_3\text{L}]$ compounds (174). In the case of $\text{P}(\text{OC}_6\text{H}_5)_3$, a product of another type is $\{\text{MnI}(\text{NO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]_2\}$ (184). Displacement of halogen from the complex anions, *cis*- $[\text{MnX}_2(\text{CO})_4]^-$ with $\text{P}(\text{C}_6\text{H}_5)_3$ gives the products, *cis*- $[\text{MnX}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$, $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CN}$, which react with excess base to yield *trans*- $\{\text{MnX}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$. The disubstituted product is obtained more readily with $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ as the base (185).

Careful studies of the kinetics of the reactions between bases and the carbonyl halides and the properties of the products have been carried out. It has been established that the CO exchange reaction of $[\text{MnX}(\text{CO})_5]$ compounds proceeds by an $\text{S}_{\text{N}}1$ reaction, with one carbonyl group (that *trans* to X) exchanging more slowly than the others, and with the over-all rate of exchange decreasing with changing X in the order $\text{Cl} > \text{Br} > \text{I}$ (55, 56). The reaction of $[\text{MnX}(\text{CO})_5]$ with a ligand to give $[\text{MnX}(\text{CO})_4\text{L}]$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{As}(\text{C}_6\text{H}_5)_3, \text{Sb}(\text{C}_6\text{H}_5)_3, \text{C}_2\text{H}_5\text{NC}, \text{PCl}_2\text{C}_6\text{H}_5, \text{P}(\text{OC}_4\text{H}_9)_3, \text{P}(\text{OCH}_2)_3\text{CCH}_3, \text{P}(\text{OC}_6\text{H}_5)_3$, also takes place by an $\text{S}_{\text{N}}1$ mechanism, with rates decreasing in the order $\text{Cl} > \text{Br} > \text{I}$ (62). In both the CO exchange and the substitution reaction the rate-determining step is dissociation of a carbonyl group, and the rates are essentially the same (62). The chloride compound reacts most rapidly because the chloride's greater electronegativity leaves less *d*-electron density (higher positive charge) on the manganese atom; hence, less metal-carbon double bonding occurs, and the metal-carbon bond is more easily broken. The carbonyl group *trans* to the halide ion, which exchanges much more slowly than the other four, has less competition for the π -donor capacity of the filled *d* orbital of proper symmetry for it than do the carbonyl groups *trans* to one another.

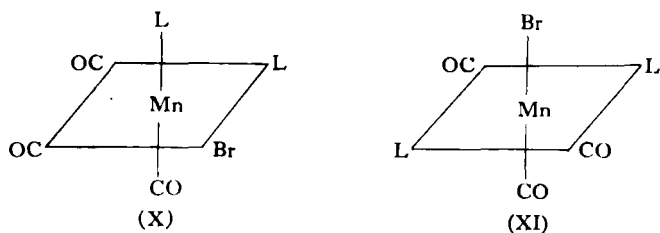
More basic ligands, including pyridine, aniline, *p*-toluidine, and tributylphosphine, give directly the disubstituted compounds, $[\text{MnX}(\text{CO})_3\text{L}_2]$ (62). The rate of the reaction between $[\text{MnX}(\text{CO})_4\text{L}]$ (VIII) and a second ligand L' to give $[\text{MnX}(\text{CO})_3\text{LL}']$ (IX) is independent of the nature and concentration of L' , so again a dissociative mechanism is involved. The rate of reaction decreases as one varies the initial ligand L in the order



This order corresponds to that of decreasing bulkiness. Since the axial CO *trans* to X is tightly held, and the products (IX) are in the configuration with L, L', and X mutually *cis*, the more labile CO groups in $[\text{MnX}(\text{CO})_4\text{L}]$ (VIII) must be those *trans* to another CO. This is consistent with the effect of increased M—C π -bonding in the less-labile CO groups *trans* to ligands other than CO (63).



However, despite the more favorable M—C bond energies in the *cis* compounds, conversion of the *cis*- $[\text{MnBr}(\text{CO})_3\text{L}_2]$ species to *trans* isomers does occur, again by an $\text{S}_{\text{N}}1$ path (60, 61). The ligands which most readily form the *trans* isomer are those with the greatest π -bonding tendencies, which serve to stabilize the activated complex. Steric effects are also important; only the *trans* isomer can be prepared with triphenylphosphine as ligand (61), contrary to an earlier report (176). Both isomers have been isolated for $\text{L} = \text{P}(\text{OC}_6\text{H}_5)_3$ and made *in situ* for $\text{L} = \text{P}(\text{OC}_4\text{H}_9)_3$, $\text{P}(\text{C}_4\text{H}_9)_3$, and $\text{PCl}_2\text{C}_6\text{H}_5$. The isomers probably have the configurations (X) and (XI) (60, 61).



A study of the carbon monoxide exchange reactions of $[\text{MnCl}(\text{CO})_3\text{L}_2]$ shows a decrease of rate in the order $\text{P}(\text{C}_6\text{H}_5)_3 \gg \text{As}(\text{C}_6\text{H}_5)_3 \gg \text{Sb}(\text{C}_6\text{H}_5)_3$,

although infrared spectra indicate that the ligands are involved to the same degree in double bonding to the metal (56). Exchange is rapid for $L = \text{Te}(\text{C}_6\text{H}_5)_2$, but very slow for $L = \text{NH}_3$, *o*-phen (56). In the reaction of $[\text{MnX}(\text{CO})_3\text{L}_2]$ with nitric oxide, again the rates decrease in the order $\text{P}(\text{C}_6\text{H}_5)_3 > \text{As}(\text{C}_6\text{H}_5)_3 > \text{Sb}(\text{C}_6\text{H}_5)_3$ (56).

e. *Derivatives of Organomanganese Carbonyls.* The methyl- or phenyl-manganese pentacarbonyls $[\text{MnR}(\text{CO})_5]$ react with primary or secondary amines to give acyl manganese derivatives of composition $[\text{Mn}(\text{COR})(\text{CO})_4(\text{NHR}'\text{R}'')]$, $\text{R} = \text{CH}_3$; $\text{NHR}'\text{R}'' = \text{NH}_2\text{C}_6\text{H}_{11}$, NH_3 , $\text{NH}(\text{CH}_3)(\text{C}_6\text{H}_{11})$, $\text{NH}_2\text{C}_6\text{H}_5$; and $\text{R} = \text{C}_6\text{H}_5$; $\text{NHR}'\text{R}'' = \text{NH}_2\text{C}_6\text{H}_{11}$, $\text{NH}_2\text{C}_6\text{H}_5$ (117). Treatment of the acetylmanganese (cyclohexylamine) derivative with sodium methoxide yields the sodium salt of the $[\text{Mn}(\text{CO})_4(\text{NH}_2\text{C}_6\text{H}_{11})]^-$ anion, which reacts with methyl iodide with redistribution of ligands to form $[\text{MnI}(\text{CO})_3(\text{NH}_2\text{C}_6\text{H}_{11})_2]$ of the well-known type previously discussed (186). Dispute exists as to the exact mechanism of this type of reaction, in which basic attack causes a carbonyl group to be apparently inserted into the $\text{H}_3\text{C}-\text{Mn}$ bond, i.e., $[\text{MnCH}_3(\text{CO})_5] \rightarrow [\text{Mn}(\text{COCH}_3)(\text{CO})_4\text{L}]$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, RNH_2 , R_2NH (186 a-c).

Lewis bases have been found to react readily with cyclopentadienyl-manganese tricarbonyl, particularly when the mixture is irradiated with ultraviolet light. Only one carbonyl group is usually replaced, giving straightforwardly the products $[\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_2\text{L}]$, $\text{L} = \text{py}$ (187), $\text{C}_6\text{H}_5\text{NH}_2$ (188), CH_3CN (189), $\text{C}_6\text{H}_5\text{CN}$ (122), $\text{C}_6\text{H}_{11}\text{NC}$ (188), $\text{C}_5\text{H}_{10}\text{NH}$ (188), piperazine (190), urotropine (190), $\text{P}(\text{C}_6\text{H}_5)_3$ (12, 191, 192, 193), $\text{As}(\text{C}_6\text{H}_5)_3$ (12, 188, 191), $\text{Sb}(\text{C}_6\text{H}_5)_3$ (188), $\text{P}(\text{OC}_6\text{H}_5)_3$ (192), $\text{P}(\text{C}_4\text{H}_9)_3$ (192), $\text{P}(\text{C}_3\text{H}_7)_3$ (192), $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$ (192), $(\text{CH}_3)_2\text{SO}$ (194, 194a), $(\text{CH}_2)_4\text{SO}$ (194a), $(\text{C}_6\text{H}_5)_2\text{SO}$ (194a), $(\text{CH}_2\text{O})_2\text{SO}$ (194a), $(\text{CH}_3\text{O})_2\text{SO}$ (188), SO_2 (188, 194a), $\text{S}(\text{C}_2\text{H}_5)_2$ (188, 194a), $\text{S}(\text{CH}_2)_4$ (194a), $\text{S}(\text{C}_6\text{H}_5)_2$ (194a), SH_2 (194a), $\text{C}_3\text{H}_7\text{NH}_2$ (195), $\text{C}_6\text{H}_{13}\text{NH}_2$ (195), $(\text{CH}_3)_2\text{NH}$ (195), $(\text{CH}_3)_3\text{N}$ (195), pyrrolidine (195), quinoline (195), dimethylpyrrolidine (195), NH_3 (195). The analogous compounds $[\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)(\text{CO})_2\text{L}]$ have been reported, with $\text{L} = \text{C}_5\text{H}_{10}\text{NH}$ (196), py (187), $\text{P}(\text{C}_6\text{H}_5)_3$ (12, 191, 192), $\text{As}(\text{C}_6\text{H}_5)_3$ (12, 191), $\text{P}(\text{OCH}_3)_3$ (192), $\text{P}(\text{OC}_6\text{H}_5)_3$ (192), and $\text{As}(\text{C}_2\text{H}_5)_3$ (192).

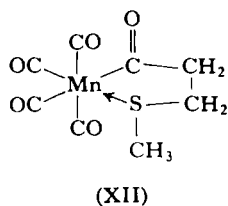
The disubstituted compounds $[\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})\text{L}_2]$ have been described, with $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (193, 197), $(\text{CH}_3)_2\text{SO}$ (194), $\text{Sb}(\text{CH}_2\text{C}_6\text{H}_5)_3$ (192), $\text{P}(\text{CH}_3)_2$ (192), and $\text{P}(\text{OCH}_3)_3$ (192); analogous $[\text{Mn}(\text{C}_5\text{H}_4\text{CH}_3)(\text{CO})\text{L}_2]$ species have been listed for various ligands (192). A patent, which claims

such materials for use as antiknock additives in gasoline and as herbicides, also refers to the use of other ligands and other alkyl cyclopentadienyl derivatives (192).

Bidentate ligands give, under mild conditions, bridged dimers $[(C_5H_5)(CO)_2Mn(LRL)Mn(C_5H_5)(CO)_2]$, $LRL = 1,2$ -bis(diphenylphosphino)ethane (12, 191), diarsine (12, 191), piperazine (190), and triethylenediamine (190). The methylcyclopentadienyl analogs have been isolated for $LRL =$ diphosphine or diarsine (12, 191). Prolonged irradiation of these mixtures forms chelated monomers of the type $[Mn(C_5H_5)(CO)(LRL)]$, $LRL =$ diphosphine, diarsine; also known are the methylcyclopentadienyl analogs (12, 191). A number of oxygen donors certainly react with $[Mn(C_5H_5)(CO)_3]$ and $[Mn(C_5H_4CH_3)(CO)_3]$, but the preliminary products are unstable and cannot be isolated (197). The reaction of PCl_3 and $AlCl_3$ with $[Mn(C_5H_5)(CO)_3]$ yields an interesting compound of the above type, $[(CO)_3Mn(C_5H_4PCl_2)Mn(C_5H_5)(CO)_2]$, in which L in the standard formula $[Mn(C_5H_5)(CO)_2L]$ is $[Mn(C_5H_4PCl_2)(CO)_3]$ (198). The ligands $P_2(CH_3)_4$, $P_2(C_6H_5)_4$, and $As_2(CH_3)_4$ also give the simple bridged species $[(C_5H_5)(CO)_2Mn(E_2R_4)Mn(CO)_2(C_5H_5)]$ (198a).

In the photochemical synthesis of $[Mn(C_5H_5)(CO)_2L]$ from $[Mn(C_5H_5)(CO)_3]$ the quantum yield is one (139, 197). The infrared spectra and stability of the substituted compounds have been discussed (188, 195). The reaction apparently has a dissociative mechanism, and the rate of carbon monoxide evolution decreases with changing L in the order $C_6H_8 > CH_3CN > N(C_2H_5)_3 > CH_3COCH_3 > C_6H_5C\equiv CC_6H_5 > py > C_2H_5OOCCH_3 > (CH_2)_4O$ (138). The stability of the products depends primarily on the donor strength of the ligand; the order of stability with the $[Mn(C_5H_5)(CO)_2]$ moiety is the same that one finds with acceptors of the type of BF_3 (195). From comparative studies of the photochemical synthesis with acetonitrile one may arrange complex acceptors in the order $\{Cr(CO)_2[p-C_6H_4(COOH)_2]\} \simeq [Cr(CO)_5] > [Mn(C_5H_5)(CO)_2] > [Cr(CO)_2(C_6H_6)] > \{Cr(CO)_2[C_6H_3(CH_3)_3]\}$ (189).

An example of a compound with bridging nitrosyl groups has been obtained by reduction of the cation $[Mn(C_5H_5)(CO)_2(NO)]^+$ with sodium borohydride, giving a product of composition $[Mn(C_5H_5)(CO)(NO)]_2$, a "pseudo- $[Fe(C_5H_5)(CO)_2]_2$ " which has both terminal and bridging carbonyl and nitrosyl groups, and may be a mixture of isomers (199, 200). An unusual manganese compound (XII) is prepared from $Na[Mn(CO)_5]$ and $ClCH_2CH_2SCH_3$ (152).



2. Rhenium

Fewer examples are known of compounds of rhenium than of manganese, but the behavior of the two carbonyls is quite similar. The reaction between $[\text{Re}_2(\text{CO})_{10}]$ and $\text{P}(\text{C}_6\text{H}_5)_3$ produces only the dimer $[\text{Re}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]_2$, in contrast to the case of manganese (17). High-pressure carbonylation of triphenylphosphine-rhenium(II) halide species leads at 50°C to $[\text{ReX}_2\text{COL}_2]$, at 120°C to reduced pentacoordinate $[\text{ReX}(\text{CO})_2\text{L}_2]$, and at 200°C to $[\text{ReX}(\text{CO})_3\text{L}_2]$, $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (201); the latter is the only one of the series with a manganese analog. A copper catalyst facilitates the reduction of the halide, permitting one to use a rhenium(III) halide initially (202). The iodide complex $\{\text{ReI}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ accepts only one molecule of carbon monoxide, yielding $\{\text{ReI}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (202).

In view of the later finding that the halorhenium phosphine complexes were at first incorrectly formulated, e.g., $\{\text{ReCl}_3[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ is in fact $\{[\text{ReOCl}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2]\}$ (202a), and that oxygen and nitrogen are frequently found in the rhenium complexes (202b, 202c) the exact formulation of the carbonylated products is somewhat questionable.

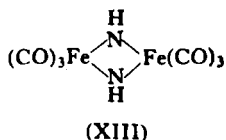
The rhenium carbonyl halides react with donors as do their manganese analogs. Rhenium pentacarbonyl chloride reacts with liquid ammonia to form the neutral complex $[\text{ReCl}(\text{CO})_4(\text{NH}_3)]$, which reacts with *o*-phenanthroline at 60°C to give $[\text{ReCl}(\text{CO})_3(o\text{-phen})]$. Another product is the ionic material $[\text{Re}(\text{CO})_4(\text{NH}_3)_2]^+\text{Cl}^-$, which reacts with pyridine at 120°C to give $[\text{ReCl}(\text{CO})_3(\text{py})_2]$ (203). The iodide analog of the latter compound has been obtained by direct reaction of pyridine with $[\text{ReI}(\text{CO})_4]_2$ or $[\text{ReI}(\text{CO})_5]$ (204). The reaction between *p*-tolyl isocyanide and the pentacarbonyl chloride affords the ionic complex $[\text{Re}(\text{CO})_4\text{L}_2]^+\text{Cl}^-$, $\text{L} = \text{CH}_3$, $\text{C}_6\text{H}_4\text{NC}$ (203). The compounds $[\text{ReX}(\text{CO})_3\text{L}_2]$, with $\text{X} = \text{Cl}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, py (176), $\text{C}_6\text{H}_5\text{NH}_2$ (203); and $\text{X} = \text{I}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, py , and dipy (176) have been obtained from the direct reaction. Further substitution takes place upon treatment of $\{\text{ReX}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ with *p*-tolylisocyanide, giving $\{\text{ReX}(\text{CO})(\text{RNC})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, $\text{X} = \text{Cl}, \text{Br}$ or

under more drastic conditions a hexacoordinate species $\{\text{ReCl}(\text{CO})(\text{RNC})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (201). The reaction between $[\text{ReCl}(\text{CO})_5]$ and phenyl mercaptan gives a sulfur-bridged species, $[\text{Re}(\text{SC}_6\text{H}_5)(\text{CO})_4]_2$ (205). Substituted rhenium(I) carbonyl cations $[\text{Re}(\text{CO})_4\text{L}_2]^+$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, *o*-phen are obtained, as are their manganese analogs, from the high-pressure and high-temperature reaction of $[\text{ReCl}(\text{CO})_3\text{L}_2]$ with AlCl_3 , FeCl_3 , or ZnCl_2 and carbon monoxide (181).

E. Iron, Ruthenium, and Osmium

1. Iron

a. *The Direct Reaction of the Carbonyl with Bases.* The displacement of carbonyl groups bonded to iron may be readily accomplished by treatment with nitrogen-donor ligands, but disproportionation usually occurs, so that complex iron cations and unsubstituted carbonylferrate anions are the products (3). In the cases of *N*-phenyl-2-pyridinaldimine (206), piperidine (207), pyrrolidine (207), and *o*-phenanthroline (208, 209), this conversion proceeds by preliminary formation of an adduct of iron pentacarbonyl with one or more molecules of base, e.g., the dark blue complex $[\text{Fe}(\text{CO})_5(\text{o-phen})]$ (208, 209). Indirect methods have furnished iron carbonyl complexes with nitrogen-iron bonds. Treatment of $[\text{HFe}(\text{CO})_4]^-$ with $[\text{NH}_2\text{OSO}_3]^-$ gives $[\text{Fe}(\text{CO})_4\text{NH}_3]$, as well as traces of a bridged imino compound



$[\text{Fe}(\text{NH})(\text{CO})_3]_2$ (155, 210) (XIII). The latter compound is more satisfactorily prepared from sodium nitrite and tetracarbonylferrate(−II) anion (155, 211, 212). Even at very low temperatures, the combination of ammonia and iron carbonyls gives no complexes (213).

Ligands containing phosphorus, arsenic, or antimony as the donor atom do not cause disproportionation of iron carbonyls, and fairly stable, simple substitution products are obtained. The direct reaction, carried out either thermally or photochemically, with any of the three iron carbonyls, has yielded the complexes $[\text{Fe}(\text{CO})_4\text{L}]$, with $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (12, 35, 214, 215, 125a), $\text{P}[\text{N}(\text{CH}_3)_2]_3$ (71), pentaphenylphosphole (216, 217), $\text{As}(\text{C}_6\text{H}_5)_3$ (12,

215, 215a), $\text{Sb}(\text{C}_6\text{H}_5)_3$ (215); and *trans*- $[\text{Fe}(\text{CO})_3\text{L}_2]$, with $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (12, 35, 214, 215, 215a), $\text{P}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2$ (218), $\text{P}[\text{N}(\text{CH}_3)_2]_3$ (71), $\text{As}(\text{C}_6\text{H}_5)_3$ (12, 215, 215a), and $\text{Sb}(\text{C}_6\text{H}_5)_3$ (215). All the mixed complexes $[\text{Fe}(\text{CO})_n(\text{PF}_3)_{5-n}]$ ($n = 1-4$) are accessible by the direct reaction (218a). Chelating ligands forming *cis*- $[\text{Fe}(\text{CO})_3\text{L}_2]$ species include *o*-phenylenebis(dimethylarsine) (12, 215a, 219), 1,2-bis[di(cyanoethyl)phosphino]ethane (220), 1,2-bis(diphenylphosphino)ethane (215a, 218, 220), and 1,2-bis(diphenylarsino)ethane (220). Only with *o*-phenylenebis(dimethylarsine) has a monocarbonyl complex $[\text{Fe}(\text{CO})\text{L}_2]$ been described (219). These bidentate ligands can function as bridges between two monosubstituted iron moieties, e.g., in $[(\text{CO})_4\text{FeP}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_2(\text{C}_6\text{H}_5)_2\text{PFe}(\text{CO})_4]$ (12, 215a, 218). Frequently tricarbonyl(diene)iron complexes are more satisfactory starting materials than the iron carbonyls themselves (218, 220).

Protonation of the mono- or bis(triphenylphosphine) or -(triphenylarsine)iron carbonyl compounds in 98% sulfuric acid gives metal hydride species detectable by NMR techniques, and showing a P—H coupling, but defying isolation (67, 68). Since protonation of the phosphine-iron carbonyl complexes increases the CO stretching frequency (68), suggesting the presence of a weaker metal-carbon bond in these materials, their reactions have become of interest (59). Small amounts of trifluoroacetic acid promote very rapid CO exchange (after an induction period) in the normally inert pentacarbonyliron and tetracarbonyl(triphenylphosphine)iron, and less-rapid exchange in tricarbonylbis(triphenylphosphine)iron, which undergoes other, complicating reactions. Interestingly, the latter compound is the only one of these in the case of which IR analysis detects a metal-hydrogen bond under these conditions. In concentrated sulfuric acid, which protonates both substituted carbonyls, no exchange is observed. The failure of protonated tricarbonylbis(triphenylphosphine)iron to undergo exchange is consistent with the position of its CO stretching frequency, which still lies near those of *unprotonated* $[\text{Fe}(\text{CO})_5]$ and $[\text{Fe}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ (59).

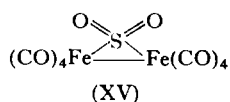
Tetraalkylbiphosphines or -biarsines react with $[\text{Fe}(\text{CO})_5]$ to give two classes of compounds, P- or As-bridged dimers $[\text{FeER}_2(\text{CO})_3]_2$ (XIV), $\text{ER}_2 = \text{P}(\text{CH}_3)_2$ (125, 126), $\text{P}(\text{C}_2\text{H}_5)_2$ (125), $\text{As}(\text{CH}_3)_2$ (125, 126), $\text{As}(\text{CF}_3)_2$



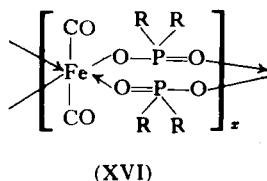
(147), and, under milder conditions (125) or with $[\text{Fe}_3(\text{CO})_{12}]$ (126), a binuclear complex retaining the P—P bond, $[(\text{CO})_4\text{FeP}_2(\text{CH}_3)_4\text{Fe}(\text{CO})_4]$. The reaction of $[\text{Fe}(\text{CO})_5]$ with $\text{PCl}(\text{C}_6\text{H}_5)_2$ gives what must be a binuclear complex $[(\text{CO})_4\text{FeP}_2(\text{C}_6\text{H}_5)_4\text{Fe}(\text{CO})_4]$ (221). From $[\text{Fe}(\text{CO})_5]$ and $\text{PI}(\text{CF}_3)_2$ one may prepare a compound $\{\text{Fe}_2\text{I}[\text{P}(\text{CF}_3)_2](\text{CO})_6\}$, which probably has a structure corresponding to (XIV) (164).

The reaction between iron carbonyls and isonitriles leads simply to the products $[\text{Fe}(\text{CO})_4\text{CNR}]$ and *trans*- $[\text{Fe}(\text{CO})_3(\text{CNR})_2]$, $\text{R} = \text{CH}_3$, C_2H_5 , *p*- $\text{C}_6\text{H}_4\text{OCH}_3$ (222), *t*- C_4H_9 (35). The monosubstituted compound only has been obtained for $\text{R} = \text{C}_6\text{H}_5$ (222), $(\text{CH}_3)_3\text{Si}$, $(\text{CH}_3)_3\text{Ge}$, $(\text{CH}_3)_3\text{Sn}$ (223). A binuclear species $[(\text{CO})_4\text{Fe}(\text{CNC}_6\text{H}_4\text{NC})\text{Fe}(\text{CO})_4]$ has been described (222), as have mixed species $[\text{Fe}(\text{CO})_3(\text{CNR})(\text{CNR}')]$ (224). An unusual route to $[\text{Fe}(\text{CO})_4\text{CNC}_6\text{H}_5]$ is by reaction between dodecacarbonyltriiron and phenyl isocyanate or phenyl isothiocyanate (225).

Metal carbonyl derivatives with metal-oxygen bonds are not common. Flash photolysis of oxygen-iron pentacarbonyl mixtures produces a substance believed to be $[\text{Fe}_2\text{O}_2(\text{CO})]$ (226). Sulfur trioxide and iron pentacarbonyl afford an unisolable material thought to be the pyrophosphate $\{\text{Fe}[\text{O}(\text{SO}_3)_2](\text{CO})_3\}$ (141). However, the reaction between sulfur dioxide and enneacarbonyldiiron gives a substance $[\text{Fe}_2(\text{CO})_8\text{SO}_2]$, for which

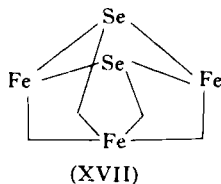


structure (XV) has been proposed, as well as a compound, $[\text{Fe}_3\text{S}_2(\text{CO})_9]$ (discussed later) (227). Diphenylphosphinic acid and iron pentacarbonyl upon irradiation furnish low polymers with repeating units of the type (XVI) (142).



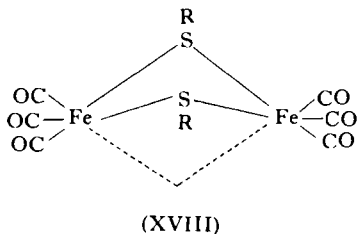
Compounds having iron bonded to carbonyl groups as well as to sulfur atoms are numerous, varied, and well studied. The known role of sulfur and selenium as promoters of the high-pressure synthesis of iron pentacarbonyl

has led to the attempt to isolate possible iron carbonyl chalcogenide intermediates (228, 229). A convenient synthesis of such materials is by the reaction of tetracarbonylferrate anion and sulfurous, selenious, or tellurous acid; the products are of the type $[\text{Fe}_3\text{X}_2(\text{CO})_9]$, $\text{X} = \text{S}, \text{Se}, \text{Te}$ (229). A single-crystal X-ray study of $[\text{Fe}_3\text{Se}_2(\text{CO})_9]$ establishes its structural



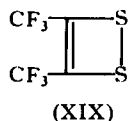
framework as (XVII), in which an $[\text{Fe}_2\text{Se}_2(\text{CO})_6]$ fragment of idealized $C_{2v}-2mm$ symmetry is bonded to an $[\text{Fe}(\text{CO})_3]$ fragment by two bent $\text{Fe}-\text{Se}$ bonds and two bent $\text{Fe}-\text{Fe}$ bonds. The heavy atom framework forms a square pyramid, slightly distorted so that all $\text{Fe}-\text{Se}$ distances are equal (230). The $[\text{Fe}_2\text{Se}_2(\text{CO})_6]$ fragment has the same type of structure as $[\text{Fe}(\text{SC}_2\text{H}_5)(\text{CO})_3]_2$ (16). The compound $[\text{Fe}_3\text{Se}_2(\text{CO})_9]$ is isomorphous with the originally reported (229) $[\text{Fe}_3\text{S}_2(\text{CO})_9]$ (230). However, recently the reaction of dodecacarbonyltriiron with cyclohexene episulfide or 3-chloropropylene episulfide has given an apparently isomeric compound of composition $[\text{Fe}_3\text{S}_2(\text{CO})_9]$ (231).

Oxidation of the tetracarbonylferrate anion with polysulfide (229) or hyposulfite (211) ion leads to a compound of another stoichiometry, $[\text{Fe}_2\text{S}_2(\text{CO})_6]$. One may similarly obtain the analogous compound, $[\text{Fe}_2\text{Se}_2(\text{CO})_6]$ (13). Alkyl and aryl sulfur moieties bond readily with iron carbonyls, forming sulfur-bridged compounds of the type $[\text{Fe}(\text{SR})(\text{CO})_3]_2$

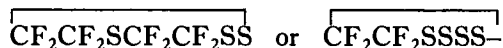


(XVIII) (13), a structure markedly similar to (XIV). The structure (XVIII) in which the Fe_2X_2 ring is nonplanar is common to both the species

$[\text{FeX}(\text{CO})_3]_2$ and $[\text{Fe}(\text{XR})(\text{CO})_3]_2$ (13), $\text{X} = \text{S}, \text{Se}$. This structure, first suggested on the basis of infrared and dipole moment evidence (13), has been completely verified by X-ray studies of such species (16, 231a). The first route to a $[\text{Fe}(\text{SR})(\text{CO})_3]_2$ species was the reaction between iron(II) salts, alkaline ethyl mercaptan, and carbon monoxide (232). The reaction between iron carbonyls and mercaptans has given such compounds with $\text{R} = \text{C}_6\text{H}_5$ (233, 234, 235), C_2H_5 (233, 234), α -naphthyl, or β -naphthyl (234). Alkyl sulfides and iron carbonyls have given this type of product for $\text{R} = \text{CH}_3$ or C_2H_5 (234). Diphenyl disulfide and iron carbonyls give $[\text{Fe}(\text{SC}_6\text{H}_5)(\text{CO})_3]_2$ (234), but in the case of the reaction between dimethyl disulfide and dodecacarbonyltriiron, two isomeric products of composition $[\text{Fe}(\text{SCH}_3)(\text{CO})_3]_2$ have been isolated and shown to be different by their NMR spectra (69). The X-ray structure determination of $[\text{Fe}(\text{SC}_2\text{H}_5)(\text{CO})_3]_2$ clearly shows the possibility of the existence of stereoisomers differing in the orientation of the ethyl groups with respect to the rest of the molecule (16). This possibility has been realized in the methyl derivatives (69). Mercaptobenzothiazole reacts with triiron dodecacarbonyl to give a material of composition $[\text{Fe}_3(\text{CH}_2\text{S}_2)(\text{CO})_{10}]$ (234). Triiron dodecacarbonyl and diethyldiselenide form a complex $[\text{Fe}(\text{SeC}_2\text{H}_5)(\text{CO})_3]_2$ (13), strictly analogous to the sulfur compounds already discussed. Compounds related to the $[\text{Fe}(\text{SR})(\text{CO})_3]_2$ species, but having the two sulfur atoms linked by a carbon chain are somewhat more readily formed than are those from monodentate groups. The chelated ones are obtained from the reactions between iron carbonyls and 3,4-toluenedithiol, 1,2-ethanedithiol, and bis(trifluoro-



methyl)dithietene (XIX) (236). Dodecacarbonyltriiron and the cyclic polysulfides



give a similar $[\text{Fe}_2(\text{CO})_6]$ derivative with an $\text{SCF}_2\text{CF}_2\text{S}$ bridging group (236). The use of *o*-aminobenzenethiol as a reagent produces a complex $[\text{Fe}_2(\text{SC}_6\text{H}_4\text{NH})(\text{CO})_6]$, with both RS and RNH bridging groups (237).

A mixed cobalt-iron carbonyl sulfide (238) is discussed in Section F, 1, a.

The reaction between $[\text{FeBr}_2(\text{CO})_4]$ and $\text{Na}[\text{S}_2\text{CN}(\text{CH}_3)_2]$ leads to a compound $\{\text{Fe}[\text{S}_2\text{CN}(\text{CH}_3)_2]_2(\text{CO})_2\}$ containing two four-membered rings (169b).

Diphenyltellurium reacts with triiron dodecacarbonyl to give a complex which is not like the products from aryl sulfur compounds, but a simple substitution product of the formula $[\text{Fe}(\text{CO})_4\text{Te}(\text{C}_6\text{H}_5)_2]$. Treatment of tetracarbonylferrate anion or triiron dodecacarbonyl with bis(*p*-anisyl)-tellurium produces the tellurium-bridged species $[\text{Fe}(\text{TeC}_6\text{H}_4\text{OCH}_3)(\text{CO})_3]_2$ analogous to the sulfur-containing compounds (165). Reaction between the complexes $[\text{FeSR}(\text{CO})_3]_2$ and *o*-phenanthroline gives mixed complexes $[\text{FeSR}(\text{CO})(o\text{-phen})]_2$ (233, 234). The reactions between tertiary phosphines and the selenium complexes $[\text{Fe}(\text{SeR})(\text{CO})_3]_2$ have been described (239).

An unusual group of covalent compounds includes $[\text{Fe}_3\text{As}_2(\text{CO})_{11}]$, $[\text{Fe}_2\text{Sb}(\text{CO})_8]$, and $[\text{Fe}_5\text{Bi}_2(\text{CO})_{20}]$ obtained by treatment of tetracarbonylferrate ion with compounds of the trivalent metalloids. These products have very complicated structures, presumably bridged through the Group V atoms (240).

b. *Nitrosyl-Carbonyl Derivatives.* The well-known dicarbonyldinitrosyl-iron, $[\text{Fe}(\text{CO})_2(\text{NO})_2]$, can be prepared by the treatment of iron carbonyls with nitric oxide (241), by reaction between the tetracarbonylferrate anion and nitrous acid (242), or most advantageously by reaction between nitrosyl chloride and iron pentacarbonyl (243). The direct combination of bases with $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ can give displacement of both carbonyl groups, with formation of $[\text{Fe}(\text{NO})_2\text{L}_2]$ species (244), $\text{L} = \text{CNR}$ (224), $\text{P}(\text{C}_6\text{H}_5)_3$ (245, 246, 247), $\text{P}(\text{OC}_6\text{H}_5)_3$ (246), $\text{As}(\text{C}_6\text{H}_5)_3$ (243), $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$ (243). However, with care one may also obtain the monosubstituted derivatives, $[\text{Fe}(\text{CO})(\text{NO})_2\text{L}]$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (243), $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_4\text{-CH}_3)_3$ (246), $\text{Sb}(\text{C}_6\text{H}_5)_3$ (246, 247), $\text{Sb}(\text{C}_6\text{H}_4\text{CH}_3)_3$ (246), $\text{Te}(\text{C}_6\text{H}_5)_2$ (165). The treatment of $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ with $\text{P}_2(\text{CH}_3)_4$, $\text{P}_2(\text{C}_6\text{H}_5)_4$, $\text{As}_2(\text{CH}_3)_4$ (248), or $\text{As}_2(\text{CF}_3)_4$ (147) yields the ER_2 -bridged species, $[\text{FeER}_2(\text{NO})_2]_2$, with the Fe_2E_2 ring planar, in contrast to the situation with the S- and E-bridged carbonyl species. One carbonyl-containing species, $[(\text{NO})_2(\text{CO})\text{-FeP}_2(\text{CH}_3)_4\text{Fe}(\text{CO})(\text{NO})_2]$, has been isolated from this type of reaction (248). Treatment of the ER_2 -bridged complexes $[\text{FeER}_2(\text{CO})_3]_2$ with nitric oxide leads to no new complexes (248).

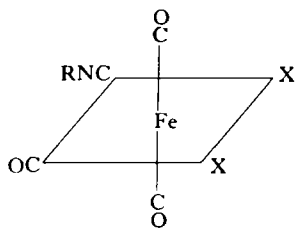
The anion $[\text{Fe}(\text{CO})_3(\text{NO})]^-$, isoelectronic with $[\text{Fe}(\text{CO})_2(\text{NO})_2]$, can be

obtained by the action of alcoholic sodium hydroxide or sodium amalgam in tetrahydrofuran on $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ (249, 250). Another route to this anion is the action of nitrite ion on the tetracarbonylferrate anion (251). The infrared spectrum of $[\text{Fe}(\text{CO})_3\text{NO}]^-$ shows that (as expected) it has more metal-carbon double-bond character than the isoelectronic and isostructural $[\text{Co}(\text{CO})_3\text{NO}]$ (252). Once formed, the $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ anion undergoes a number of reactions. Acidification at low temperature yields a hydride $[\text{FeH}(\text{CO})_3\text{NO}]$, which decomposes at -45°C to $[\text{FeH}_2(\text{CO})_4]$ and $[\text{Fe}(\text{CO})_2(\text{NO})_2]$. Reaction with nitrous acid leads again to $[\text{Fe}(\text{CO})_2(\text{NO})_2]$. Mercuric cyanide or salts of arsenic, antimony, bismuth, thallium, and tin give covalent derivatives, e.g., $\text{Hg}[\text{Fe}(\text{CO})_3(\text{NO})]_2$ and $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_3(\text{NO})]_2$ (251).

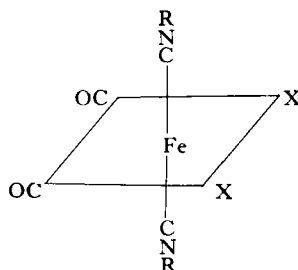
The reactions of $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$ are very similar to those of the isoelectronic compound, $\text{Hg}[\text{Co}(\text{CO})_4]_2$. Pyridine causes disproportionation of $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$, as do ethylenediamine and *p*-methoxyphenyl isocyanide (253). The mercury derivative reacts with certain ligands to give stable complexes $\text{Hg}[\text{Fe}(\text{CO})_2(\text{NO})\text{L}]_2$, where $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (253, 254), $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{Sb}(\text{C}_6\text{H}_5)_3$ (253), or $\text{P}[\text{N}(\text{CH}_3)_2]_3$ (254). Under more drastic conditions the ionic complex $[\text{Fe}(\text{CO})_2\text{NO}(\text{tdp})_2]^+[\text{Fe}(\text{CO})_3\text{NO}]^-$, where $\text{tdp} = \text{P}[\text{N}(\text{CH}_3)_2]_3$, may be obtained, or ultimately the carbonyl-free material $[\text{Fe}(\text{NO})_2(\text{tdp})_2]$ (254). In the NMR spectrum of the latter compound, which is tetrahedral, the P—P coupling is much smaller than in the spectra of *trans*-bis(phosphine) five- or six-coordinate structures (254). Other heavy metal derivatives of the $[\text{Fe}(\text{CO})_3\text{NO}]^-$ anion likewise undergo substitution by suitable bases, giving, e.g., $\text{Sn}[\text{Fe}(\text{CO})_2(\text{NO})\text{L}]_4$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, and $\text{Cd}[\text{Fe}(\text{CO})_2(\text{NO})\text{L}]_2$, $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$. These phosphine- or arsine-containing complexes are more stable than their precursors (253). Tetramethylbiphosphine and $\text{Hg}[\text{Fe}(\text{CO})_3\text{NO}]_2$ produce a complex mixture of products, including those also obtained from the ligand and $[\text{Fe}(\text{CO})_2(\text{NO})_2]$ (248).

c. Derivatives of the Carbonyl Halides. The halogenation under mild conditions of iron carbonyl-base complexes yields stable complexes, e.g., $[\text{FeI}_2(\text{CO})_2(\text{py})_2]$ (255), $\{\text{FeI}_5(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (215), and $[\text{Fe}(\text{C}_3\text{F}_7)\text{I}(\text{CO})_2(\text{diphosphine})]$ (218). Careful oxidation of $[\text{Fe}(\text{CO})_3(\text{diarsine})]$ with one equivalent of iodine gives the unusual five-coordinate, paramagnetic complex $[\text{FeI}(\text{CO})_2(\text{diarsine})]$, while use of an excess of iodine or bromine gives $[\text{FeI}_2(\text{CO})_2(\text{diarsine})]$ (219). An infrared spectroscopic study has shown that halogenation in ether of $[\text{Fe}(\text{CO})_4\text{CNR}]$ gives products of the

composition $[\text{FeX}_2(\text{CO})_3\text{CNR}]$ (XX), whereas the same treatment of $[\text{Fe}(\text{CO})_3(\text{CNR})_2]$ gives $[\text{FeX}_2(\text{CO})_2(\text{CNR})_2]$ (XXI), with $\text{X} = \text{Cl}, \text{Br}, \text{I}$;



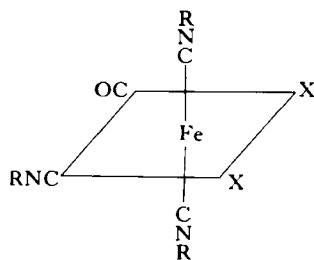
(XX)



(XXI)

and $\text{R} = t\text{-C}_4\text{H}_9$, $p\text{-C}_6\text{H}_4\text{CH}_3$ (53). Bromine or iodine easily breaks the metal-metal bond in $[\text{FeER}_2(\text{CO})_3]_2$, forming $[\text{FeX}(\text{ER}_2)(\text{CO})_3]_2$, $\text{X} = \text{Br}, \text{I}$; $\text{ER}_2 = \text{P}(\text{CH}_3)_2$, $\text{As}(\text{CH}_3)_2$, in which the methyl groups are all equivalent, although they are nonequivalent in the starting material (126).

Bases displace carbon monoxide from the carbonyl halides to give products like those obtained from the halogenation of base complexes. The appropriate halides $[\text{FeX}_2(\text{CO})_4]$ and bases have given $[\text{FeX}(\text{CO})_3\text{L}]$ with $\text{X} = \text{Cl}$ and $\text{L} = t\text{-C}_4\text{H}_9\text{NC}$, $p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$ (53); $\text{X} = \text{Br}$ and $\text{L} = t\text{-C}_4\text{H}_9\text{NC}$, $p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$ (53), $\text{Te}(\text{C}_6\text{H}_5)_2$ (165); and $\text{X} = \text{I}$ and $\text{L} = \text{CH}_3\text{NC}$ (224), $t\text{-C}_4\text{H}_9\text{NC}$, $p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$ (53), $\text{Te}(\text{C}_6\text{H}_5)_2$ (165), $\text{Sb}(\text{C}_6\text{H}_5)_3$ (247), $\text{P}(\text{OC}_6\text{H}_5)_3$ (244); $[\text{FeX}_2(\text{CO})_2\text{L}_2]$ with $\text{X} = \text{Cl}$ and $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{Sb}(\text{C}_6\text{H}_5)_3$, alkyl and aryl phosphates (247); $\text{X} = \text{Br}$ and $\text{L} = \text{P}(\text{C}_6\text{H}_{11})_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, $\text{Sb}(\text{C}_6\text{H}_5)_3$, alkyl and aryl phosphates (247), diarsine (219); $\text{X} = \text{I}$ and $\text{L} = \text{py}$, $o\text{-phen}$, $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$ (256), diarsine (219), CH_3NC (224); $[\text{FeX}_2(\text{CO})(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_3]$ with $\text{X} = \text{Cl}, \text{Br}, \text{I}$

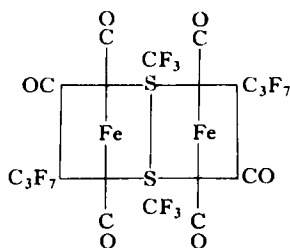


(XXII)

(53), structure (XXII); and $[\text{FeI}_2(\text{CO})(p\text{-CH}_3\text{OC}_6\text{H}_4\text{NC})_3]$ (224). Considering perfluoroalkyl groups as pseudohalogens (7), one may cite the following products from the reaction of ligand and iron carbonyl halide: $[\text{Fe}(\text{C}_3\text{F}_7)\text{I}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$; $[\text{Fe}(\text{C}_3\text{F}_7)\text{I}(\text{CO})_2\text{L}_2]$ with $\text{L} = \text{py}$, dipy (257), diphosphine (218); $[\text{Fe}(\text{C}_3\text{F}_7)_2(\text{CO})_2\text{L}_2]$, $\text{L} = \text{py}$, dipy (257); and $[\text{Fe}(\text{CF}_2)_4(\text{CO})_2(\text{diphosphine})]$ (218).

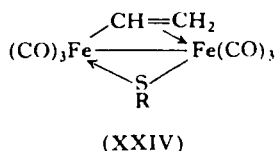
A third route to substituted iron carbonyl halides is by carbonylation of phosphine-metal halide complexes. This reaction [its facility depending upon the steric requirements of the phosphine employed, and decreasing, in the order $\text{P}(\text{C}_2\text{H}_5)_3 > \text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5 \gg \text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2 \gg \text{P}(\text{C}_6\text{H}_5)_3$ (258); $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2 \gg \text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2$ (218)] has given the *cis* complexes $[\text{FeX}_2(\text{CO})_2\text{L}_2]$, $\text{X} = \text{Cl}$; $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$, $\text{P}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2$ (258), diphosphine (218); and $\text{X} = \text{Br}$, I , NCS ; $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$ (258). When reduced with metal hydrides or metal alkyls in the presence of carbon monoxide this type of complex $[\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2$, diphosphine] affords the known tricarbonylbis(phosphine) complexes. Preliminary carbonylation or even formation of the phosphine-metal halide complex is not necessary; reduction of a mixture of metal halide and phosphine in the presence of carbon monoxide gives $[\text{Fe}(\text{CO})_3\text{L}_2]$ and $[\text{Fe}(\text{CO})_4\text{L}]$ (218). *Cis-trans* isomerization of $[\text{FeCl}_2(\text{CO})_2\text{L}_2]$ has been noted under mild conditions for $\text{L} = (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, but not for $\text{L} = \text{PC}_2\text{H}_5(\text{C}_6\text{H}_5)_2$ (218).

While no $[\text{FeSR}_f(\text{CO})_3]_2$ compounds with simple R_fS bridging groups have been prepared, the treatment of $[\text{Fe}(\text{C}_3\text{F}_7)\text{I}(\text{CO})_4]$ with CF_3SAg permits the isolation of a compound of composition $[\text{Fe}(\text{C}_3\text{F}_7)(\text{SCF}_3)(\text{CO})_3]_2$. In the proposed structure (XXIII), the presence of the C_3F_7 groups on iron removes the need to postulate a metal-metal bond to explain the observed diamagnetism (236).

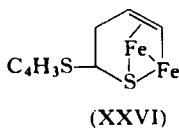
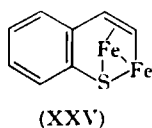


(XXIII)

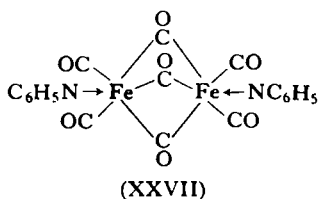
d. *Derivatives of Organoiron Carbonyls.* The treatment of tricarbonyl-(diene)iron complexes and related materials with bases such as triphenylphosphine has frequently been used as a method of displacing the organic ligand to aid in characterization of the complex (259). The other product of the reaction is then a well-known complex, such as $[\text{Fe}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3]$ or $\{\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$. Under milder conditions, mixed carbonyl(base)-(hydrocarbon)iron complexes may be isolated, e.g., $[\text{Fe}(\text{CO})_2(\text{C}_4\text{H}_6)\text{L}]$, $\text{L} = \text{P}(\text{OC}_2\text{H}_5)_3$, $\text{PC}_6\text{H}_5(\text{OR})_2$ (260); $[\text{Fe}(\text{CO})_2(\text{C}_8\text{H}_8)(\text{As}(\text{C}_6\text{H}_5)_3)]$ (259); $[\text{Fe}(\text{CO})_3(\text{maleic anhydride})\text{P}(\text{C}_6\text{H}_5)_3]$ (261); $[\text{Fe}(\text{CO})_2(\text{cyclopentadienone})\text{P}(\text{C}_6\text{H}_5)_3]$ (262); $[\text{Fe}(\text{CO})_2(\text{tropone})\text{P}(\text{C}_6\text{H}_5)_3]$ (263); $[\text{Fe}(\text{CO})_2(2,5\text{-methoxy-1-tricarbonylferrate})(\text{SO}_2)]$ (227), and $[\text{FeX}(\text{CO})_2(\pi\text{-C}_3\text{H}_5)\text{P}(\text{C}_6\text{H}_5)_3]$, $\text{X} = \text{Br}, \text{I}$ (264). Certain organosulfur compounds form iron carbonyl derivatives which apparently have sulfur-metal bonds as well as bonds from hydrocarbon moieties. These compounds were discovered in work stimulated by the finding that sulfur-containing carbonyl compounds were formed in the desulfurization of thiophene with iron carbonyl (265). Alkyl vinyl sulfides form complexes believed to be of the type (XXIV). Related com-



pounds are the thianaphthene derivative with the framework (XXV) (19) and the 2,2'-dithienyl derivative with the framework (XXVI) (237).



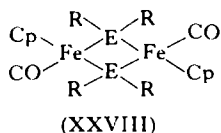
Phenyl isocyanate or phenyl azide and iron carbonyls combine to form an unusual complex of possible structure (XXVII).



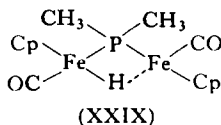
The butyl analog has been prepared. Triphenylphosphine replaces one mole of carbon monoxide per iron atom, without rupturing the ring, forming $\{\text{Fe}_2(\text{CO})_3(\text{C}_6\text{H}_5\text{NCO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (225).

Tetracarbonyldi(π -cyclopentadienyl)diiron $[\text{FeCp}(\text{CO})_2]_2$ ($\text{Cp} = \text{C}_5\text{H}_5$), and its simple derivatives also undergo base-substitution reactions. Treatment of $[\text{FeClCp}(\text{CO})_2]$ with CO and $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, or $\text{Sb}(\text{C}_6\text{H}_5)_3$ affords the complex cations $[\text{FeCp}(\text{CO})_2\text{L}]^+$. Reduction of $[\text{FeCp}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3]^+$ with sodium borohydride furnishes a neutral complex, $[\text{Fe}(\text{CO})_2(\text{C}_5\text{H}_6)\text{P}(\text{C}_6\text{H}_5)_3]$ (266). A contrasting reaction, in that a carbonyl group is replaced, but the halide ion is retained, is that between $[\text{FeICp}(\text{CO})_2]$ and phenyl isocyanide; the products are $[\text{FeICpCO}(\text{C}_6\text{H}_5\text{NC})]$ and $[\text{FeICp}(\text{C}_6\text{H}_5\text{NC})_2]$ (150, 267). The corresponding chloride and bromide complexes give no complexes which retain carbonyl groups (150). Similarly, $[\text{FeICp}(\text{CO})_2]$ and $\text{P}(\text{C}_6\text{H}_5)_3$ give in addition to the ionic species, $[\text{FeCp}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3]^+$, the covalent $[\text{FeICp}(\text{CO})\text{P}(\text{C}_6\text{H}_5)_3]$ (150). Tris(dimethylamino)phosphine and $[\text{FeICp}(\text{CO})_2]$ give only the ionic material $[\text{FeCp}(\text{CO})_2\text{tdp}]^+\text{I}^-$. Alkylation of $\text{K}[\text{Fe}(\text{CN})_2\text{CpCO}]$ with activated organic iodides or bromides gives, e.g., $[\text{FeCNCpCO}(\text{CNR})]$ and then $[\text{FeCpCO}(\text{CNR})_2]$ ($\text{R} = \text{allyl}$) (151).

The tetraalkyl and tetraarylphosphines and biarsines react with $[\text{FeCp}(\text{CO})_2]_2$ to give the ER_2 -bridged dimers $[\text{FeCpER}_2\text{CO}]_2$ (XXVIII)



(14). These complexes can also be obtained from the reaction between $[\text{FeCp}(\text{CO})_2]\text{Na}$ and EClR_2 . Stereoisomers of $[\text{FeCpP}(\text{CH}_3)_2\text{CO}]_2$ have been detected; they differ in the relative orientation of the methyl groups. An unusual by-product of one of these reactions is (XXIX), which has only

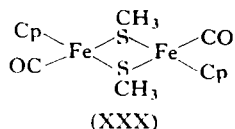


one bridging PR_2 group. Of course, the hydrogen atom is probably associated with both iron atoms and is effectively a bridging group (14) [cf. (VII)].

An interesting variation is observed in the reaction between $[\text{FeCp}(\text{CO})_2]_2$ and $\text{As}_2(\text{CF}_3)_4$. Since the $\text{As}(\text{CF}_3)_2$ group is a weaker donor than $\text{As}(\text{CH}_3)_2$, the primary product of this reaction is a monomeric complex, $[\text{FeCpAs}(\text{CF}_3)_2(\text{CO})_2]$, in which the $\text{As}(\text{CF}_3)_2$ group acts as a pseudohalogen. Upon irradiation the normal, bridged complex $[\text{FeCpAs}(\text{CF}_3)_2\text{CO}]_2$ is formed (147).

The halide $[\text{FeBrCp}(\text{CO})_2]$ reacts with $\text{P}_2(\text{CH}_3)_4$ and $\text{As}_2(\text{CH}_3)_4$ to give the ionic [compare the behavior of $\text{P}(\text{C}_6\text{H}_5)_3$] single-bridged complex $[\text{FeCp}(\text{CO})_2\text{ER}_2\text{FeCp}(\text{CO})_2]^+\text{Br}^-$ (268). Treatment of $[\text{FeBrCp}(\text{CO})_2]$ with KCN in aqueous ethanol yields the ionic product $\text{K}_2[\text{Fe}(\text{CN})_2\text{CpCO}]$, which can be alkylated with activated organic bromides or iodides to give isonitrile complexes, e.g., $[\text{FeCpCN}(\text{CO})(\text{CNC}_3\text{H}_5)]$ and $[\text{FeCpCO}(\text{CNC}_3\text{H}_5)_2]\text{Br}$ (207). Potassium cyanide and $[\text{FeCp}(\text{CO})_2]_2$ afford the complex $\text{K}_2[\text{Fe}(\text{CN})_2\text{Cp}(\text{CO})]$ (207).

From $[\text{FeCp}(\text{CO})_2]$ and CH_3SSCH_3 , a sulfur-bridged complex (XXX)



may be obtained (19). The RS- (XXX) and $-\text{ER}_2$ (XXVIII) bridged compounds are clearly analogous. The reaction between $\text{Na}[\text{FeCp}(\text{CO})_2]$ and $\text{ClCH}_2\text{CH}_2\text{SCH}_3$ leads to a normal alkylated product $[\text{FeCp}(\text{CH}_2\text{CH}_2\text{SCH}_3)(\text{CO})_2]$, which on irradiation yields $[\text{FeCp}(\text{CO})_2]_2$, $[\text{FeCp}(\text{SCH}_3)(\text{CO})]_2$ (XXX), an acyl compound $[\text{FeCp}(\text{COCH}_2\text{CH}_2\text{SCH}_3)\text{CO}]$, and an unusual nonbridged methyl thio compound, $[\text{FeCp}(\text{SCH}_3)(\text{CO})_2]$, which can also be prepared by the reaction between CH_3SSCH_3 and $[\text{FeHCp}(\text{CO})_2]$. The complex $[\text{FeCp}(\text{SCH}_3)(\text{CO})_2]$ is alkylated exothermically with methyl iodide to give an ionic complex of dimethyl sulfide $[\text{FeCp}(\text{CO})_2\text{S}(\text{CH}_3)_2]^+\text{I}^-$ (152). Thus the normally bridging groups $-\text{SR}$ (152) and $-\text{AsR}_2$ (147) can function as pseudohalogens.

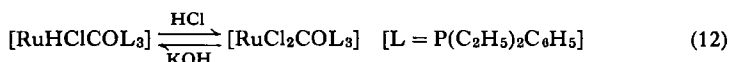
An interesting new development is the finding that SO_2 may be inserted in metal-carbon bonds just as CO may be, e.g. $[\text{FeCpR}(\text{CO})_2] \rightarrow [\text{FeCp}(\text{RSO}_2)(\text{CO})_2]$ (268a).

2. Ruthenium and Osmium

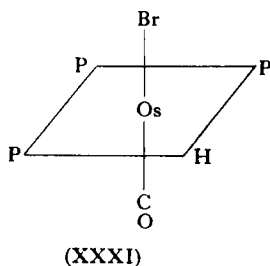
Perhaps because of their relative unavailability the simple carbonyls of ruthenium and osmium have not been reported to combine with basic

ligands. However, the polymeric complex $[\text{RuI}_2(\text{CO})_2]$ reacts with bases to give quite stable materials of composition $[\text{RuI}_2(\text{CO})_2\text{L}_2]$, $\text{L} = \text{NH}_3$ (269), py (269, 270), $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$, $\text{C}_6\text{H}_5\text{NH}_2$, CH_3CN , dipy , $\text{AsCH}_3(\text{C}_6\text{H}_5)_2$ (269), $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, and $\text{Sb}(\text{C}_6\text{H}_5)_3$ (270).

The tendency of the heavier transition metals to exhibit readily variable valence states and coordination numbers is demonstrated by a series of remarkable and facile preparations of ruthenium and osmium carbonyl compounds, in which carbonyl and hydride groups are derived from alcohols (271–276). If one boils the simple or complex halides of ruthenium or osmium in the presence of a tertiary phosphine or arsine, in a suitable alcohol, e.g., $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, $\text{CH}_2=\text{CHCH}_2\text{OH}$, or $\text{C}_2\text{H}_5\text{OH}$ containing KOH , one may isolate a number of types of complexes, many containing hydride and/or carbonyl groups. The systems are very complicated, and a frequent product is of the type $[\text{MHXCOL}_3]$, which reacts further as shown in Eq. (12) (271), with loss of hydrogen. Compounds of other “platinum-



group” elements, including rhenium, rhodium, and iridium, are known to undergo similar reactions. One detailed paper has appeared, on which the following discussion is based (275). The compounds of formulation $[\text{OsHXCOL}_3]$, $\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$ are best made by treatment of $(\text{NH}_4)_2\text{OsX}_6$, $\text{X} = \text{Cl}, \text{Br}$ with the ligand in a suitable alcoholic solvent. Reference (275) gives the exact reaction conditions used for best results. The products are air-sensitive in solution but exceedingly stable in the crystalline state. Although other evidence, particularly infrared spectra, shows conclusively the presence of hydrides, the NMR spectra show no sign of a characteristic metal-hydride resonance where it is usually found. The deuterated compounds have been made, and labeling experiments have shown that the solvent is the source of the carbonyl groups in these com-



plexes. The exact courses of the reactions remain a subject for investigation. Certainly they are among the most unusual processes found in organometallic chemistry. A single-crystal X-ray structure of $\{\text{OsHBrCO}[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ indicates octahedral coordination with the hydride ion occupying a normal position (XXXI) (276).

A detailed study of the hydridocarbonylation of ruthenium compounds has now appeared (276a).

F. Cobalt, Rhodium, and Iridium

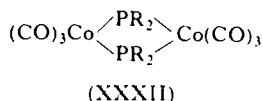
1. Cobalt

a. *The Direct Reaction of the Carbonyl with Bases.* Strong bases cause ready disproportionation of cobalt carbonyls, forming, e.g., $[\text{Co}(\text{py})_6]^{2+}[\text{Co}(\text{CO})_4]_2^-$ (3). Nine electrons short of the krypton configuration, cobalt might be expected to form base-carbonyl complexes found as paramagnetic monomers, diamagnetic dimers, or diamagnetic ions. These types of behavior have indeed been observed.

Triphenylphosphine reacts with octacarbonyldicobalt in nonpolar solvents to give the simple product of substitution of one carbonyl group on each cobalt atom, $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$, but in polar solvents disproportionation occurs, producing $\{\text{Co}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+[\text{Co}(\text{CO})_4]^-$ (17, 277–281). The cation of this complex is isoelectronic and isostructural with the neutral species $\{\text{Fe}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (280). The tetramer $[\text{Co}_4(\text{CO})_{12}]$ also combines with triphenylphosphine, forming $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$ (282). An interesting solvent effect is found when $\text{Co}_2(\text{CO})_8$ is treated with $\text{P}(\text{C}_6\text{H}_5)_3$ in Nujol. The products include not only the two previously mentioned complexes, but a new one, $[\text{Co}_2(\text{CO})_7\text{P}(\text{C}_6\text{H}_5)_3]$ (283). The two cobalt atoms in this material (283) and in $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]_2$ (280) are linked only by a metal-metal bond, although $\text{Co}_2(\text{CO})_8$ displays bridging carbonyls. The analogous ionic compounds $[\text{Co}(\text{CO})_3\text{L}_2]^+[\text{Co}(\text{CO})_4]^-$ have been similarly obtained with the ligands $\text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, and $\text{Sb}(\text{C}_6\text{H}_5)_3$, although in the latter two cases this complex decomposes at 0°C to the $[\text{Co}(\text{CO})_3\text{L}]_2$ species (17). The $[\text{Co}(\text{CO})_3\text{L}]_2$ complexes have also been prepared directly in pentane with $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, and $\text{Sb}(\text{C}_6\text{H}_5)_3$ (17), and in benzene with $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(p\text{-ClC}_6\text{H}_4)_3$, $\text{P}(p\text{-FC}_6\text{H}_4)_3$ (281), $\text{P}(\text{OC}_6\text{H}_5)_3$ (281, 245).

When mixed, $\text{Co}_2(\text{CO})_8$ and $\text{P}(\text{C}_6\text{H}_5)_3$ proceed at a rate too fast to be measured at 0°C to an addition complex, $[\text{Co}_2(\text{CO})_8\text{P}(\text{C}_6\text{H}_5)_3]$, which then

undergoes first-order decomposition at a slower rate to $[\text{Co}_2(\text{CO})_7\text{P}(\text{C}_6\text{H}_5)_3]$ which reacts rapidly with additional ligand to give the final products (66). Only the ionic product $[\text{Co}(\text{CO})_3(\text{tdp})_2]^+[\text{Co}(\text{CO})_4]^-$ may be isolated from the reaction of $[\text{Co}_2(\text{CO})_8]$ and $\text{P}[\text{N}(\text{CH}_3)_2]_3$, although traces of a covalent species may be detected (71). The chelating ligand 1,2-bis(diphenylphosphino)ethane and $[\text{Co}_2(\text{CO})_8]$ give an ionic material $[\text{Co}_2(\text{CO})_4(\text{diphosphine})_3]^{2+}[\text{Co}(\text{CO})_4]^{2-}$; the cation, of which other salts can be prepared, has no bridging carbonyl groups (159). Tetraphenylbiphosphine and $[\text{Co}_2(\text{CO})_8]$ react to afford a product of composition $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_2]_2$, which probably has structure (XXXII), although there is some uncertainty about the molecular weight (161, 221).



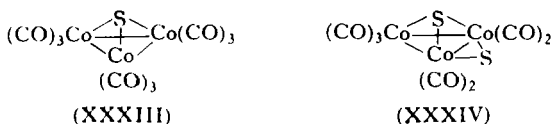
The same material can be prepared from the combination of $\text{Na}[\text{Co}(\text{CO})_4]$ with $\text{PCl}(\text{C}_6\text{H}_5)_2$ (161, 284). When tetramethylbiphosphine and $[\text{Co}_2(\text{CO})_8]$ are heated, the only isolable product is the novel compound $\{\text{Co}_3[\text{P}(\text{CH}_3)_2]_2(\text{CO})_7\}$, which is diamagnetic and has both terminal and bridging carbonyl groups. The several possible structures involve a triangular array of cobalt atoms (161). The treatment of $\{\text{Co}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+[\text{Co}(\text{CO})_4]^-$ with LiCl , LiBr , or KCNS in boiling acetone produces yet another polymeric material, which has been formulated as $\{\text{Co}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\}_n$ (285).

The neutral cobalt carbonyl-phosphine complexes are very easily reduced by sodium amalgam to the corresponding anions (with the krypton configuration), as is cobalt carbonyl itself (286, 287). Acidification of $\text{Na}^+[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]^-$ gives a hydride $[\text{CoH}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$, which is more stable but less acidic than $[\text{CoH}(\text{CO})_4]$ (286, 287). The phosphine-substituted hydride and the anions $[\text{Co}(\text{CO})_3\text{PR}_3]^-$, $\text{R} = \text{C}_6\text{H}_5$, OC_6H_5 , react with metal salts, forming covalent compounds of cadmium, zinc, tin, thallium, copper, silver, and, most significantly, mercury, e.g., $\text{Hg}[\text{Co}(\text{CO})_3\text{L}]_2$ (286, 287). The chemical properties of the phosphinetricarbonylcobalt hydride, anion, and mercury derivatives are quite like those of the corresponding tetracarbonylcobalt compounds.

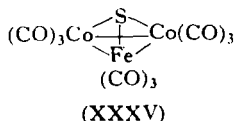
The mercury compounds $\text{Hg}[\text{Co}(\text{CO})_3\text{L}]_2$, $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, and $\text{Sb}(\text{C}_6\text{H}_5)_3$, may also be obtained by treatment of mercury tetracarbonylcobaltate $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with the ligand in

acetone, although trimethyl phosphite under these conditions yields only metallic mercury and $[\text{Co}(\text{CO})_3\text{P}(\text{OCH}_3)_3]_2$ (282). With benzene as solvent, the direct reaction of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with $\text{P}[\text{N}(\text{CH}_3)_2]_3$ gives $\text{Hg}[\text{Co}(\text{CO})_3(\text{tdp})]_2$ (71). The zinc, cadmium, tin, and thallium derivatives of $[\text{Co}(\text{CO})_4]^-$ also give substitution products containing the $[\text{Co}(\text{CO})_3\text{L}]$ group (282). The use of Nujol as a reaction medium permits the isolation from a mixture of $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and $\text{P}(\text{C}_6\text{H}_5)_3$ of an unstable monosubstituted compound $\text{Hg}[\text{Co}(\text{CO})_4][\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ (283).

The known catalytic effect of sulfur in the synthesis of cobalt carbonyl from the metal and carbon monoxide and the inhibiting effect of sulfur compounds on the oxo reaction have pointed the way to the existence of a number of cobalt carbonyl derivatives containing sulfur. Elemental sulfur (288, 289, 290) and hydrogen sulfide (291) have been shown to react with $[\text{Co}_2(\text{CO})_8]$ in alkane solvents at room temperature, yielding complexes of composition $[\text{Co}_2\text{S}(\text{CO})_5]_n$, $[\text{Co}_3\text{S}(\text{CO})_9]$ (288, 289, 290), and $[\text{Co}_3\text{S}_2(\text{CO})_7]$ (290). The action of CO at higher temperatures and pressures on $[\text{Co}_2\text{S}(\text{CO})_5]_n$ gives the trimeric species, which also are obtained by acidification of a mixture of sulfite and tetracarbonylcobaltate ions (288, 290). The infrared spectrum of $[\text{Co}_3\text{S}(\text{CO})_9]$ suggests structure (XXXIII), which contains the familiar triangular array of metal atoms (288, 290). For $[\text{Co}_3\text{S}_2(\text{CO})_7]$, structure (XXXIV) has been proposed (290).



The combination under pressure of synthesis gas ($2\text{CO}/\text{H}_2$) with $[\text{Fe}(\text{CO})_5]$, $[\text{Co}_2(\text{CO})_8]$, and either thiophene, ethyl mercaptan, or sulfur itself gives a mixed-metal compound, $[\text{FeCo}_2\text{S}(\text{CO})_9]$, which may also be prepared by treatment of $[\text{Fe}_2\text{S}_2(\text{CO})_6]$ with $[\text{Co}_2(\text{CO})_8]$. This stable



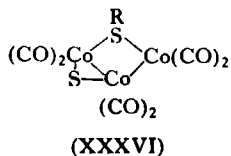
material apparently has a structure (XXXV) like that of $[\text{Co}_3\text{S}(\text{CO})_9]$ (XXXIII) (238). Little is known of another polymeric complex $[\text{Co}_4(\text{CO})_{10}]$

CS_2], which has no bridging carbonyl groups and is prepared directly from CS_2 and $[\text{Co}_2(\text{CO})_8]$ (292).

The reaction of mercaptans with cobalt carbonyl has long been known to give sulfur-bridged complexes of the type $[\text{CoSR}(\text{CO})_3]_2$, with $\text{R} = \text{C}_2\text{H}_5$, C_6H_5 (233). The compound $[\text{Co}(\text{SC}_2\text{H}_5)(\text{CO})_3]_2$ reacts further with *o*-phenanthroline to give monomeric $[\text{Co}(\text{SC}_2\text{H}_5)(\text{CO})_2(\text{o-phen})]$ (233).

The carbonylation under mild conditions of $\text{Co}(\text{SC}_2\text{H}_5)_2$ leads to a mono-carbonyl species $[\text{Co}(\text{SC}_2\text{H}_5)_2\text{CO}]_4$ (292a).

Recent studies of the action of mercaptans and dialkyl sulfides on cobalt carbonyls in hexane have led to less simple species. A 1/1 mixture of $\text{C}_2\text{H}_5\text{SH}$ or $\text{C}_2\text{H}_5\text{SSC}_2\text{H}_5$ and $[\text{Co}_2(\text{CO})_8]$ yields $[\text{Co}_4(\text{SC}_2\text{H}_5)_3(\text{CO})_7]$, from which excess mercaptan displaces more CO to furnish $[\text{Co}_4(\text{SC}_2\text{H}_5)_7(\text{CO})_5]$. These species, having several terminal and bridging carbonyl bands in the infrared, obviously have very elaborate structures, perhaps related to that of $[\text{Co}_4(\text{CO})_{12}]$. Whereas ethyl mercaptan thus displaces CO primarily, benzyl mercaptan first undergoes desulfurization to form $[\text{Co}_3\text{S}(\text{CO})_9]$, which then undergoes substitution to form $[\text{Co}_3\text{S}(\text{SCH}_2\text{C}_6\text{H}_5)(\text{CO})_6]$. Structure (XXXVI), related to that of $[\text{Co}_3\text{S}(\text{CO})_9]$ has been suggested for the latter substance (291).

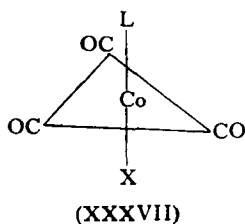


Diphenyltellurium and cobalt carbonyl react to form $[\text{Co}_2\text{Te}(\text{CO})_5]_n$, fully analogous to $[\text{Co}_2\text{S}(\text{CO})_5]_n$ (165).

b. *Nitrosyl-Carbonyl Derivatives.* The tetrahedral (293) species tricarbonylnitrosylcobalt, the preparation of which from acidified mixtures of nitrite and tetracarbonylcobaltate ions has been thoroughly studied (242, 294), undergoes ready replacement of one or two molecules of carbon monoxide. The products are a series of compounds $[\text{Co}(\text{CO})_2(\text{NO})\text{L}]$, with $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (36, 244, 295), $\text{P}(\text{OC}_6\text{H}_5)_3$ (244, 295), $\text{P}(\text{C}_6\text{H}_{11})_3$, $\text{As}(\text{C}_6\text{H}_5)_3$, (295), $\text{Sb}(\text{C}_6\text{H}_5)_3$ (246, 295), $\text{As}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{As}(p\text{-ClC}_6\text{H}_4)_3$, $\text{Sb}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, and $\text{Sb}(p\text{-ClC}_6\text{H}_4)_3$ (246); or under more severe conditions $[\text{Co}(\text{CO})(\text{NO})\text{L}_2]$, with $\text{L} = \text{o-phen}$ (36, 244), py, dipy (295), $\text{P}(\text{C}_6\text{H}_5)_3$ (36, 246, 295), $\text{P}(\text{OC}_6\text{H}_5)_3$ (246, 295), $\text{P}(\text{C}_6\text{H}_{11})_3$ (295), $\text{PCl}(\text{C}_6\text{H}_5)_2$ (36), $\text{As}(\text{C}_6\text{H}_5)_3$ (295), $\text{Sb}(\text{C}_6\text{H}_5)_3$ (295), $p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$ (36), and *tert*- $\text{C}_4\text{H}_9\text{NC}$

(36). The mixed derivative $\{\text{Co}(\text{CO})(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3][\text{As}(\text{C}_6\text{H}_5)_3]\}$ has been made in a two-step reaction (295). The infrared spectra of a large number of these complexes have been studied (36). While the $[\text{Co}(\text{CO})(\text{NO})\text{L}_2]$ species resist replacement of the last carbonyl group (246, 295), carbonyl-free products have been obtained from $[\text{Co}(\text{CO})_2(\text{NO})\text{L}]$ or $[\text{Co}(\text{CO})(\text{NO})\text{L}_2]$ and mercaptans as sulfur-bridged species $[\text{CoSR}(\text{NO})\text{L}]_2$ (296). A metal-metal bond is postulated to provide for diamagnetism here (eight electrons from the ligands per Co), but not in the case of the complexes $[\text{CoSR}(\text{CO})_3]_2$ (nine electrons from the ligands per Co). Potassium cyanide reacts with $[\text{Co}(\text{CO})_3\text{NO}]$ and $[\text{Co}(\text{CO})_2(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]$ to give the corresponding ionic compounds, $\text{K}^+[\text{CoCN}(\text{CO})_2\text{NO}]^-$ (297) and $\text{K}^+[\text{CoCN}(\text{CO})(\text{NO})\text{P}(\text{C}_6\text{H}_5)_3]^-$ (295), respectively. Nitrogen dioxide causes the cleavage of all carbonyl groups from $[\text{Co}(\text{CO})_3\text{NO}]$ (298). Hydroxide ion splits the nitric oxide group from $[\text{Co}(\text{CO})_3\text{NO}]$, forming $[\text{Co}(\text{CO})_4]^-$ and other species (299).

c. *Derivatives of the Carbonyl Halides.* Triethylphosphine-cobalt halide complexes, $\{\text{CoX}_2[\text{P}(\text{C}_2\text{H}_5)_3]_2\}$, absorb carbon monoxide at room temperature and one atmosphere, giving pentacoordinate cobalt(II) compounds of composition $\{\text{CoX}_2\text{CO}[\text{P}(\text{C}_2\text{H}_5)_3]_2\}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$ (258). Contrastingly, the high-pressure carbonylation of $\{\text{CoI}_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ yields a dicarbonyl-cobalt(I) complex, $\{\text{CoI}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (285), while in the presence of copper as a halogen acceptor, the product is $\{\text{Co}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+[\text{CuI}_2]^-$ (279). The cobalt(I) complex $\{\text{CoI}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ may also be synthesized by treating $\{\text{Co}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}^+[\text{Co}(\text{CO})_4]^-$ with sodium iodide in hot acetone (285). A route to the cobalt(I) bromide analog entails high-pressure carbonylation of a mesityl compound, $\{\text{CoBr}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{C}_9\text{H}_{11})\}$ (285). Although halogens completely cleave the carbonyl groups from the $[\text{Co}(\text{CO})_3\text{PR}_3]_2$ species, the milder halogenating agents CF_3I and *N*-bromosuccinimide react with $\text{Na}^+[\text{Co}(\text{CO})_3\text{L}]^-$ giving the cobalt(I) complexes $[\text{CoX}(\text{CO})_3\text{L}]$, $\text{X} = \text{Br}, \text{I}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{P}(\text{OC}_6\text{H}_5)_3$ (300). The tricarbonylmonophosphine halides appear to be more stable than the



bis(phosphine) ones. Treatment of $[\text{CoBr}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with sodium amalgam reconverts the halo complex to the anion $[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]^-$ (300). Infrared studies show the D_{3h} structure (XXXVII) to be present in the compounds $[\text{CoX}(\text{CO})_3\text{L}]$ (285). From dipole moment studies it may be concluded only that the complexes $[\text{CoX}(\text{CO})_2\text{L}_2]$ have L groups *trans* to each other (285).

d. *Derivatives of Organocobalt Carbonyls.* Just as many alkyl, perfluoroalkyl, acyl, and perfluoroacyl derivatives of cobalt carbonyl are obtained from treatment of $\text{Na}^+[\text{Co}(\text{CO})_4]^-$ with appropriate reagents, $\text{Na}^+[\text{Co}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]^-$ has given many analogous organo derivatives of the general type $[\text{CoR}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$, R = CH_3 (286, 287), CF_3 , CF_3CO (301), C_2F_5 , and $\text{C}_2\text{F}_5\text{CO}$ (302). Arylation of $[\text{CoBr}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ with phenyllithium gives $[\text{Co}(\text{C}_6\text{H}_5)(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ (300). In general, the phosphine-substituted organocobalt compounds are much more stable than their analogs containing only carbonyl groups and the organic group (286, 287, 301, 302). The stability and ready formation of the $[\text{CoR}(\text{CO})_3\text{L}]$ species from the ligands and perfluoroalkyl (302), alkyl, acyl, allyl (303), and other tetracarbonylcobalt compounds, have led to the use of tertiary phosphines, notably triphenylphosphine, for isolating derivatives of intermediates in studies of the mechanism of many cobalt carbonyl-catalyzed organic reactions (64, 65, 66, 303–310).

The mass of this work lies beyond the scope of this review, but a few prominent points may be cited. In most cases, treatment of either an alkyl or an acyl tetracarbonyl cobalt complex with triphenylphosphine gives only the acyl derivative, $[\text{Co}(\text{COR})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$ (304, 306). The reactions of acyl, allyl, and hydridocobalt tetracarbonyl or acetylenedicobalt hexacarbonyl complexes with phosphines are first order in the cobalt complex, so a dissociation mechanism prevails (64, 65, 66). However, the reaction between $[\text{Co}(\text{CO})_3\text{NO}]$ and $\text{P}(\text{C}_6\text{H}_5)_3$ is second order (66).

While no additional tertiary phosphine can be inserted into the organocobalt complexes $[\text{CoR}(\text{CO})_3\text{PR}_3]$, in the case of the methylcobalt compound treatment with trimethyl phosphite has given further substitution, forming compounds of the type $[\text{Co}(\text{COCH}_3)(\text{CO})_2(\text{PR}_3)\text{P}(\text{OCH}_3)_3]$ with $\text{PR}_3 = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$, and $\text{P}(\text{OCH}_2)_3\text{C}_2\text{H}_5$ (TMPP) (307). In the presence of excess $\text{P}(\text{OCH}_3)_3$, the original phosphine ligand can be replaced, leaving $\{\text{Co}(\text{COCH}_3)(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}$. Treatment of the latter with base gives the expected anion of the type $[\text{Co}(\text{CO})_2\text{L}_2]^-$, which can be methylated to give $\{\text{CoCH}_3(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_2\}$. This in turn will undergo displacement

of one more mole of carbon monoxide, finally yielding $\{\text{Co}(\text{COCH}_3)\text{CO}[\text{P}(\text{OCH}_3)_3]_3\}$; corresponding reactions with trimethylolpropane phosphite (TMPP) give products which are easier to isolate. Hydrogenation of $[\text{Co}(\text{COCH}_3)(\text{CO})_2(\text{TMPP})_2]$ has given the only hydride of its class, $[\text{CoH}(\text{CO})_2(\text{TMPP})_2]$ (307). Carboalkoxy complexes of a new type $[\text{Co}(\text{COOR})(\text{CO})_3(\text{PR}_3)]$ have recently been reported (311).

The treatment of organocobalt carbonyl complexes formed from acetylene and cobalt carbonyl with phosphines also gives organocobaltcarbonylphosphine complexes, e.g., $\{\text{Co}_2(\text{CO})_4(\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5)[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (312).

The versatile ligand $\text{P}_2(\text{CH}_3)_4$ combines with $[\text{CoCp}(\text{CO})_2]$ to form a single-bridged species $[(\text{CO})\text{CpCoP}(\text{CH}_3)_2\text{P}(\text{CH}_3)_2\text{CoCp}(\text{CO})]$, although $\text{P}_2(\text{C}_6\text{H}_5)_4$ leads to the double-bridged carbonyl-free product $[\text{CoCpP}(\text{C}_6\text{H}_5)_2]_2$ (198a). When $[\text{CoCp}(\text{CO})_2]$ is treated with CH_3SSCH_3 , $[\text{CoCpSCH}_3]_2$ is formed (19).

2. Rhodium

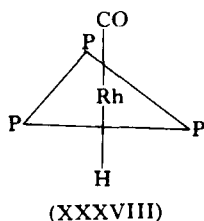
The direct reaction of rhodium carbonyl species with bases has been described only for the carbonyl halides $[\text{RhX}(\text{CO})_2]_2$ which give in a straightforward manner the *trans*-square-planar complexes $[\text{RhX}(\text{CO})\text{L}_2]$, with $\text{X} = \text{Cl}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$ (313, 314), $\text{As}(\text{C}_6\text{H}_5)_3$ (313, 314), $\text{P}(\text{C}_6\text{H}_{11})_3$ (313), $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$ (314), $\text{P}(p\text{-ClC}_6\text{H}_4)_3$ (314, 315), $\text{As}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{As}(p\text{-ClC}_6\text{H}_4)_3$, $\text{Sb}(\text{C}_6\text{H}_5)_3$, $\text{Sb}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{Sb}(p\text{-ClC}_6\text{H}_4)_3$ (314), $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{OCH}_3)_3$ (315), and $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NC}$ (316, 317); and with $\text{X} = \text{Br}$; $\text{L} = p\text{-CH}_3\text{OC}_6\text{H}_4\text{NC}$ (316). Triphenylstibine has also provided a hexacoordinate dicarbonyl complex. $[\text{RhCl}(\text{CO})_2\text{L}_3]$, and pyridine has furnished a chlorine-bridged dimer $[\text{RhCl}(\text{CO})_2(\text{py})_2]$ (313). The complexes $[\text{RhXCOL}_2]$ ($\text{X} = \text{I}, \text{SCN}$) are accessible by halogen exchange with the chlorides (315). The square-planar rhodium(I) complexes $[\text{RhX}(\text{CO})\text{L}_2]$ may be oxidized by halogens (318) or carbon tetrachloride (318a) to the hexacoordinate rhodium(III) compounds $[\text{RhX}_3(\text{CO})\text{L}_3]$ (318). This general oxidation or addition of molecules to the four-coordinate complexes of rhodium (and iridium) is further exemplified by the ready addition of activated organic halides to $[\text{RhClCO}(\text{PR}_3)_2]$ species, giving alkyl derivatives, e.g., $\{\text{RhClI}(\text{CH}_3)\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (318a).

The carbon monoxide or chlorine exchange of square-planar $\{\text{RhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ is too fast to measure, and the phosphine exchange is also exceedingly rapid (55, 58). The CO exchange by an $\text{S}_{\text{N}}1$ mechanism of the hexacoordinate $\{\text{RhCl}_3\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ is much slower. In complexes of

this type higher metal-carbon bond order is associated with higher activation energies for CO dissociation, as one might expect (57). Ethylmercaptan and $[\text{RhCl}(\text{CO})_2]_2$ condense to a sulfur-bridged species, $[\text{Rh}(\text{SC}_2\text{H}_5)(\text{CO})_2]_2$, which is cleaved by triphenylphosphine to a square-planar complex, $\{\text{Rh}(\text{SC}_2\text{H}_5)\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (319).

A further sulfur-bonded rhodium complex is the dimethyldithiocarbamate derivative *cis* $\{\text{Rh}[\text{S}_2\text{CN}(\text{CH}_3)_2](\text{CO})_2\}$ (169b).

The ability of rhodium compounds to form carbonyl derivatives directly from alcoholic solvents in the presence of tertiary phosphines provides a route to numerous complexes, as it does for compounds of iridium, ruthenium, and osmium. Thus, rhodium halide-phosphine complexes react with boiling allyl alcohol, ethanolic KOH, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, or the like, forming the already-known $[\text{RhXCOL}_2]$ compounds with $\text{X} = \text{Cl}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$ (271, 272). In the presence of excess triphenylphosphine, hydrazine converts $\{\text{RhClCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ to the pentacoordinate complex $\{\text{RhH}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ (320). The equivalence of the phosphorus atoms in the latter compound has been shown by NMR, and an X-ray study establishes the trigonal bipyramidal structure (XXXVIII) with a normal covalent $\text{Rh}-\text{H}$ bond (321).



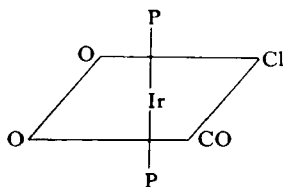
3. Iridium

Potassium halocarbonyl iridates, formed (in various stoichiometries depending on the exact reaction conditions) by combination of potassium halides, iridium halides, and carbon monoxide, react with bases to give partially substituted products (322, 323, 324). The reactions may involve reduction of Ir(III) to Ir(II) , or Ir(II) to Ir(I) , with concomitant oxidation of, e.g., I^- to I_2 . It is apparent that depending on the exact reagents and reaction conditions, different oxidation states and coordination numbers and further reactions of the initial complex may all be expected. Typical products include the chlorine-bridged species $[\text{IrCl}(\text{CO})_2(p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2)]_2$, which is in equilibrium with the monomer in solution (322); $\{\text{IrI}_2(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$

(323); $[\text{IrI}_3(\text{CO})_2\text{As}(\text{C}_6\text{H}_5)_3]$, probably of the same type as an intermediate in the other cases (323); $[\text{IrI}_3(\text{CO})(\text{NH}_3)_2]$ (324); $[\text{IrI}_2(\text{CO})(\text{NH}_3)_3]$ (324); $\{\text{IrI}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (323); and $\{\text{IrI}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (323). Bromotricarbonyliridium(I) reacts with triphenylphosphine, yielding $\{\text{IrBr}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$. The compounds $[\text{IrX}(\text{CO})_2(\text{amine})]$ react with phosphines or arsines to give unstable pentacoordinate species $[\text{IrX}(\text{CO})_2\text{L}_2]$, which lose carbon monoxide and form compounds of the type $[\text{IrX}(\text{CO})(\text{L}_2)]$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3, \text{As}(p\text{-CH}_3\text{C}_6\text{H}_4)_3, \text{Sb}(p\text{-ClC}_6\text{H}_4)_3$ (322).

Carbonylnitrosyl iridium complexes are represented by $\{\text{Ir}(\text{CO})(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ made by the action of nitric oxide on $\{\text{IrHCO}[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ (324a).

The formation of carbonyl complexes from iridium halide-phosphine mixtures in reactive solvents, such as 2-methoxyethanol, follows the lines of that from rhodium halides. For example, IrCl_3 or $(\text{NH}_4)_2[\text{IrCl}_6]$, triphenylphosphine, and alcohols interact at 190°C or above, giving $\{\text{IrClCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$; IrCl_3 , triphenylarsine, and ethylene glycol at 170°C produce $\{\text{IrHCl}_2\text{CO}[\text{As}(\text{C}_6\text{H}_5)_3]_2\}$ (325). The phosphine analog of the latter compound, $\{\text{IrHCl}_2\text{CO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ arises from addition of hydrochloric acid to $\{\text{IrClCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (325). As in the case of the rhodium analog, $\{\text{IrClCO}[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ is reduced by hydrazine to a trigonal bipyramidal complex, $\{\text{IrH}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3\}$ (320). The latter complex and its rhodium analog are, in a sense, comparable to the pentacoordinate $[\text{CoH}(\text{CO})_4]$ (320). Simple molecules readily add to the four-coordinate iridium complex $\{\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, furnishing hexacoordinate complexes, e.g., $\{\text{IrH}_2\text{Cl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, $\{\text{IrD}_2\text{Cl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, $\{\text{IrHCl}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (326), and alkyl compounds of the type $[\text{IrClX}(\text{R})\text{CO}(\text{PR}_3)_2]$ (318a). The treatment of $\{\text{IrHCl}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ with Cl_2 or excess HCl in 1,2-dimethoxyethane gives $\{\text{IrCl}_3(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ (326). A finding of potentially great significance is that $\{\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ is a reversible oxygen absorber (327). An X-ray crystallographic study shows the structure

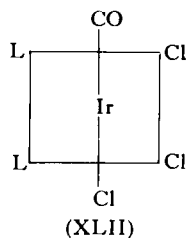
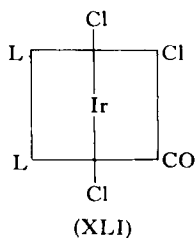
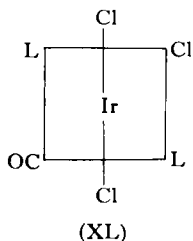


(XXXIX)

of the oxygenated compound, $\{\text{IrCl}(\text{O}_2)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ to be (XXXIX) (328). The oxygen-oxygen distance in this molecule is longer than that in O_2 , but less than that in $[\text{O}_2]^{2-}$ (328).

The complex $\{\text{IrHCl}_2(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ condenses with mercuric chloride, eliminating HCl and forming a novel compound with a mercury-iridium bond $\{\text{IrCl}_2(\text{HgCl})(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$. Direct addition of HgCl_2 or Hg_2Cl_2 to $\{\text{IrCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ also gives this material. The mercuric bromide, iodide, and acetate analogs $\{\text{IrCl}_2(\text{HgX})(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ have been similarly obtained. Thus, HgX_2 joins Cl_2 , HCl , H_2 , and O_2 as an oxidizing agent for these four-coordinate complexes of $\text{Ir}(\text{I})$. Similar mercuration has not been observed for the corresponding rhodium compounds (329).

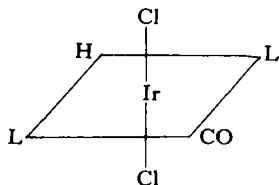
A detailed description has appeared of the reaction between a tertiary phosphine, arsine, or stibine, carbon monoxide, and chloroiridic acid (reduced *in situ* to chloroiridous acid) in 1,2-dimethoxyethane (330). The products of composition $[\text{IrCl}_3(\text{CO})\text{L}_2]$ are found in three configurations (XL), (XLI), and (XLII), depending upon the particular conditions.



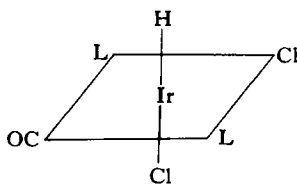
Products of the less-stable configuration (XLI) are found after short reaction times and may be converted to those of configuration (XL) on further treatment. In some cases, products of configuration (XLI) are transformed in time into those of configuration (XLII). Substances have been isolated in configuration (XL) for $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_4\text{H}_9)_3$, $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$, $\text{As}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$, and $\text{Sb}(\text{C}_3\text{H}_7)_3$; in configuration (XLI) for $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$, $\text{P}(\text{C}_4\text{H}_9)_3$, $\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$, $\text{As}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5$, and $\text{As}(\text{C}_2\text{H}_5)_3$; and in configuration (XLII) for $\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$ and $\text{P}(\text{C}_4\text{H}_9)_3$ (330). A bromide complex $[\text{IrBr}_3\text{COL}_2]$ of type (XL) has been formed by reaction between LiBr and $\{\text{IrCl}_3(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_2\}$ in boiling 1,2-dimethoxyethane.

The reaction of CO under pressure with $\{\text{IrCl}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$ or $\{\text{IrCl}_3[\text{As}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3\}$ yields the products of configuration (XLI). The

reaction of CO under pressure with $\{\text{IrCl}_3[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_3\}$ in the presence of ethanol affords, depending on conditions, two isomers (XLIII) and (XLIV) of the composition $[\text{IrHCl}_2(\text{CO})\text{L}_2]$ (330), which we have met



(XLIII)



(XLIV)

before (326). The isomer of form (XLIII) may be obtained by the action of boiling alcoholic KOH on $\{\text{IrCl}_3(\text{CO})[\text{P}(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5]_2\}$ of configuration (XLI) but not (XL). Apparently a chloride *trans* to Cl or CO is not readily cleaved from Ir, whereas the chloride *trans* to L (in XLI) is (330).

G. Nickel, Palladium, and Platinum

1. Nickel

Bases coordinating through nitrogen atoms normally stimulate disproportionation of nickel carbonyl to carbonyl-free cations and polynuclear carbonylnickelates (3). In the cases of pyridine, morpholine, α -picoline, and piperidine, this reaction has been demonstrated to proceed via a neutral complex $[\text{Ni}(\text{CO})_3\text{L}]$ (331). When the base is *o*-phenanthroline (331, 332) or dipyridyl (333) the primary product, e.g., $[\text{Ni}(\text{CO})_2(o\text{-phen})]$ (331, 332), does not disproportionate and may be isolated. Very careful work has shown that the reaction of $\text{Ni}(\text{CO})_4$ and liquid ammonia gives as intermediates nonionic compounds $[\text{Ni}(\text{CO})_3\text{NH}_3]$ and $[\text{Ni}(\text{CO})_2(\text{NH}_3)_2]$, both of which disproportionate above -60°C (334).

Nickel carbonyl reacts very readily with phosphines and similar donors. Table VI summarizes the variety of complexes prepared by the direct reaction; some of them have been identified only by infrared spectroscopy.

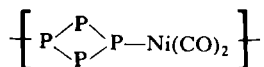
If $\{\text{Ni}(\text{CO})_2[\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]_2\}$ is allowed to react further with nickel carbonyl, one finds an unusual but ill-characterized product, $[\text{Ni}(\text{CO})\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3]$, which is believed to have no terminal carbonyl groups (342). A number of mixed phosphine complexes, $[\text{Ni}(\text{CO})_2(\text{PR}_3)(\text{PR}_3')]$, have been prepared (40). The hydride complex $[\text{Ni}_2\text{H}_2(\text{CO})_6]$ and triphenylphosphine combine in the presence of ammonia, forming $\{\text{Ni}(\text{CO})_2$

TABLE VI
 SIMPLE DERIVATIVES OF NICKEL CARBONYL

Ligand	[Ni(CO) ₃ L]	[Ni(CO) ₂ L ₂]	[Ni(CO)L ₃]
P(C ₆ H ₅) ₃	30, 40, 214	30, 40, 214, 335	—
P(CH ₃) ₃	30	30	30
P(C ₈ H ₁₇) ₃	—	72	—
P(C ₂ H ₅) ₃	30	30	—
P(C ₂ H ₅) ₂ C ₆ H ₅	—	72	—
P(C ₄ H ₉) ₃	40	40, 214	—
P(C ₂ H ₅)(C ₆ H ₅) ₂	—	72	—
P(CH ₂ CH ₂ CN) ₃	—	40	—
P(OC ₆ H ₅) ₃	30	30, 40, 245	30, 336
P(OCH ₃) ₃	30	30, 245	30
P(<i>p</i> -ClC ₆ H ₄ O) ₃	336	336	336
P(<i>p</i> -FC ₆ H ₄ O) ₃	—	336	336
P(<i>p</i> -CH ₃ OC ₆ H ₄ O) ₃	—	—	336
P(<i>p</i> -NO ₂ C ₆ H ₄ O) ₃	—	336	336
P(OC ₂ H ₅) ₃	30, 40	30, 40	30, 40, 336
P(OC ₄ H ₉) ₃	30	30	30
PH ₂ (C ₆ H ₅)	—	120	—
PCl ₃	30, 40	30, 40	30
PF ₃	30	30	30, 337
P(CF ₃) ₃	41, 338	41, 338, 339	—
PF ₂ (NR ₂)	—	119	—
(R = CH ₃ , C ₂ H ₅ , piperidyl)			
PF ₂ (OC ₃ H ₇)	—	118	—
P[N(CH ₃) ₂] ₃	—	71	—
As(C ₆ H ₅) ₃	127	127	—
As(C ₂ H ₅) ₃	127	127	—
As(OC ₂ H ₅) ₃	127	127	—
As(OCH ₃) ₃	127	127	—
As(C ₅ H ₁₀ N) ₃	127	—	—
Sb(C ₆ H ₅) ₃	214	46	—
SbCl ₃	340	—	—
Sb(C ₂ H ₅) ₃	—	46	—
SbCl(C ₂ H ₅) ₂	—	46	—
Bi(C ₂ H ₅) ₃	46	—	—
P(C≡CC ₆ H ₅) ₃	41	41	—
CH ₃ NC	47	47	47, 341
C ₂ H ₅ NC	47	47	47
C ₄ H ₉ NC	47	47	47
C ₆ H ₅ NC	48	48	48
P(OCH ₂) ₃ CCH ₃	117a	117a	117a

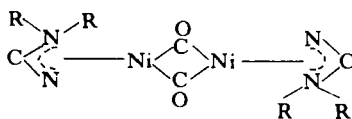
$[P(C_6H_5)_3]_2\}$ (343). Another route to phosphine-nickel carbonyl complexes is exemplified by the high-pressure carbonylations of $\{NiBr_2[P(C_6H_5)_3]_2\}$ to $[Ni(CO)_3P(C_6H_5)_3]$ (344), and of $\{Ni(NO_3)_2[P(C_6H_5)_3]_2\}$ to $\{Ni(CO)_2[P(C_6H_5)_3]_2\}$ (258). When $\{Ni(CO)_2[P(C_6H_5)_3]_2\}$ or $[Ni(CO)_3P(C_6H_5)_3]$ is treated with nitric oxide the carbonyl groups are all displaced (345).

Chelating ligands giving the complexes $[Ni(CO)_2L_2]$ include diarsine (333, 346), and the diphosphines $o-C_6H_4(PR_2)_2$ with $R = CH_3, C_2H_5, C_6H_5$ and $R_2PC_2H_4PR_2$ with $R = C_2H_5, C_6H_5$ (42, 43) and CF_3 (347). The chelating diphosphines with phenyl groups on the phosphorus atoms will react further with the disubstituted compounds, affording the $[NiL_4]$ species (43). The action of excess PF_3 upon $[Ni(CO)_2(CF_3)_2PC_2H_4P(CF_3)_2]$ produces $[NiCO(PF_3)_3]$, $[Ni(CO)_2(PF_3)_2]$, and $[NiCO(PF_3)(CF_3)_2PC_2H_4P(CF_3)_2]$ (347). The ligand $(CF_3)_2PP(CF_3)_2$ reacts with nickel carbonyl to give the binuclear complex $[(CO)_3NiP_2(CF_3)_4Ni(CO)_3]$; the analogs bridged by $P_2(C_6H_5)_4$ (126, 221), and $P_2(CH_3)_4$ (126) are similarly prepared. Upon prolonged heating $[(CO)_3NiP_2(C_6H_5)_4Ni(CO)_3]$ is converted to a diamagnetic material with two PR_2 bridges and a metal-metal bond, $[NiP(C_6H_5)_2(CO)_2]_2$ (126). Binuclear complexes prepared from potentially chelating diphosphines include $[(CO)_3NiP(C_2H_5)_2C_2H_4P(C_2H_5)_2Ni(CO)_3]$ and $\{(CO)_2Ni[P(C_2H_5)_2C_2H_4P(C_2H_5)_2]_2Ni(CO)_2\}$ (72). On treatment with nickel carbonyl, the cyclotetraphosphine $(CF_3P)_4$ gives a mixture of materials including normal derivatives of the individual phosphorus atoms, $\{(CF_3P)_4[Ni(CO)_3]_n\}$ ($n = 1, 2, 3$) and polymers apparently having backbone units



with $[Ni(CO)_3]$ end groups and $[Ni(CO)_2]$ cross links (339).

Unusual species have been obtained from the reaction between dialkyl cyanamides and $[Ni(CO)_4]$, which form $[Ni(CO)R_2NCN]_2$ complexes, ($R = CH_3, C_2H_5$) for which a pseudo- π -allylic structure (XLV) has been



(XLV)

proposed (348). The flash photolysis of oxygen–nickel carbonyl mixtures has given an ill-characterized substance $\text{NiO}(\text{CO})$ (226).

Many of these nickel carbonyl-base compounds have been prepared primarily for use in infrared studies, some of the conclusions of which are summarized briefly in Section II, C (30, 41, 46, 47, 48, 50, 51, 127, 349). The phosphine–nickel complexes have catalytic activity in the polymerization of acetylenes, and the mechanisms of these polymerizations have been studied (350, 351). Interest in these catalysts has led to an investigation of their phosphorus-31 NMR spectra, which may be qualitatively correlated with the accepted ideas on metal–ligand bonding (72).

A pioneer study in the mechanisms of metal carbonyl reactions has dealt with the exchange between complexes of the type $[\text{Ni}(\text{CO})_3\text{PR}_3]$ or $[\text{Ni}(\text{CO})_2(\text{PR}_3)_2]$ and other phosphines (40). This class of reactions proceeds by an $\text{S}_{\text{N}}1$ mechanism, the rate depending on the strength of the $\text{Ni}—\text{CO}$ or $\text{Ni}—\text{P}$ bond, which dissociates to give the tricoordinated intermediate, and hence on the nature of the phosphine originally bonded to the nickel atom. The σ -bonding ability of the phosphines seems most important in determining the strength of the $\text{Ni}—\text{P}$ bond (and the rate of reaction of the $[\text{Ni}(\text{CO})_2(\text{PR}_3)_2]$ species) and the π -bonding ability of the phosphines in determining the strength of the $\text{Ni}—\text{CO}$ bond (and the rate of reaction of $[\text{Ni}(\text{CO})_3\text{PR}_3]$ species). The nature of the added phosphine has no effect. The dissociation of CO and of PR_3 from the Ni atom are both reversible reactions (40).

Papers have considered the carbon monoxide exchange of metal carbonyls themselves (54) and of metal carbonyl halides (55) as well as of base-substituted complexes. In the series $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3]$, $\{\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2\}$, the rate of CO exchange ($\text{S}_{\text{N}}1$) decreases in the ratio 420:70:1 (54). This order clearly shows the strengthening effect of phosphine substitution on the remaining metal–carbon bond. The rate of the $\text{S}_{\text{N}}1$ reaction between $\text{P}(\text{C}_6\text{H}_5)_3$ and $[\text{Ni}(\text{CO})_4]$ is the same as the rate of CO exchange of $[\text{Ni}(\text{CO})_4]$ (66).

2. Palladium and Platinum

Although the simple carbonyls of palladium and platinum, e.g., $[\text{Pd}(\text{CO})_4]$, are not known, the carbonyl halides and some base-substituted compounds have been obtained. The reaction of carbon monoxide with the complexes $[\text{PdCl}_2(o\text{-phen})_2]$ or $[\text{PdCl}_2(\text{dipy})_2]$ in water yields very insoluble products apparently having bridging carbonyl groups (352). While carbonylation of

the alkyl or aryl complexes *trans*-{MXR[P(C₂H₅)₃]₂}, with M = Pd, Pt; X = Cl, Br, I; R = alkyl, aryl, gives only the acyl compounds *trans*-{MX(OCR)[P(C₂H₅)₃]₂} (353), the complexes [Pt₂Cl₄(PR₃)₂], with R = C₂H₅, C₃H₇, C₄H₉ absorb carbon monoxide at room temperature and one atmosphere, forming stable products of the type *cis*-[PtCl₂(CO)PR₃]. The compound [PtI₂(CO)P(C₂H₅)₃] has been similarly prepared, and the reaction between *cis*-[PtCl₂(CO)P(C₂H₅)₃] and lithium bromide gives *cis*-[PtBr₂(CO)P(C₆H₅)₃]. The carbonyl complexes are more stable than the corresponding olefin complexes (354). Carbon monoxide is taken up by the zero-valent compounds [Pt(PR₃)₄], giving [Pt(CO)₂(PR₃)₂], R = C₆H₅, *p*-ClC₆H₄ and coordinatively unsaturated {PtCO[P(*p*-ClC₆H₄)₃]₂} (355). Additional base reacts with the dicarbonyl complex, forming, e.g., {PtCO[P(C₆H₅)₃]₃} (355). Treatment of the platinum carbonyl halides, especially [PtCl₂CO]₂, with bases has given a number of mixed complexes, e.g., [PtCl₂CO(NH₃)₂], [PtCl₂COpy] (356), [PtX₂COL], X = Cl, Br, I; L = AsCH₃(C₆H₅)₂, *p*-CH₃C₆H₄NH₂, py (357, 358), and ionic [PtXCO(dipy)]⁺X⁻, X = Cl, Br, I (357, 358).

H. Metal Carbonyl Complexes with Bonds from Group III, IV, or Ib Elements

Not strictly covered by the title of this article, but cursorily mentioned for the sake of completeness are some other nonhydrocarbon derivatives of metal carbonyls. Organotin, -silicon, and -lead moieties readily bond to metal carbonyl fragments, forming such compounds as [Fe(SnR₂)(CO)₄]₂ (359), [Fe(PbR₂)(CO)₄]₂, [Fe(PbR₃)₂(CO)₄] (360–364), [Fe(SnR₃)₂(CO)₄], [Co(PbR₃)(CO)₄] (364), {SnR₂[Co(CO)₄]₂}, {SnR₂[Co(CO)₃PR₃]₂} (365), [Mn(SnR₃)(CO)₅], {SnR₂[Mn(CO)₅]₂}, [Mn(SiR₃)(CO)₅], [Mn(PbR₃)(CO)₅], [Mn(SnR₃)(CO)₄PR₃], [Mn(SnCl₃)(CO)₄PR₃] (366), {GeH₂[Mn(CO)₅]₂} (367), [FeCp(SnR₃)(CO)₂] (366), {SnCl₂[FeCp(CO)₂]₂}, [WCp(SnCl₃)(CO)₃] (368), and [Co₃(SiCH=CH₂)(CO)₉] (369). The iron carbonyl carbide [Fe₅C(CO)₁₅] deserves listing (370).

The first borane-metal carbonyl derivatives contain the rather unstable anions [Re(CO)₅(BH₃)]⁻, [Re(CO)₅(BH₃)₂]⁻, and [Mn(CO)₅BH₃]⁻, and a somewhat more stable species is [Mn(CO)₄(BH₃)P(C₆H₅)₃]. The increased stability of the phosphine-substituted borane complex suggests a role for the phosphine primarily as a σ donor, as also indicated by the NMR spectrum of [Mn(CO)₄P(C₆H₅)₃] (371). An interesting series of metal derivatives of

metal carbonyls includes $[\text{Mn}(\text{Cu-triarsine})(\text{CO})_5]$ and $[\text{Mn}(\text{Au-triarsine})(\text{CO})_5]$, with triarsine = $\text{CH}_3\text{C}[\text{CH}_2\text{As}(\text{CH}_3)_2]_3$ (372); $\{\text{Mn}[\text{AuP}(\text{C}_6\text{H}_5)_3](\text{CO})_5\}$, $\{\text{cis-Fe}[\text{AuP}(\text{C}_6\text{H}_5)_3]_2(\text{CO})_4\}$, and $\{\text{Co}[\text{AuP}(\text{C}_6\text{H}_5)_3](\text{CO})_4\}$ (373); the requirements for forming metal-metal bonds have been discussed in detail (373).

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Carboranes and Organo-Substituted Boron Hydrides

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I

INTRODUCTION AND SCOPE

Organic derivatives of boron hydrides have been known for some three decades, but only during the last few years has this area of study received widespread attention. Rapidly expanding interest in these compounds can be traced back to financial stimulation provided by various governmental agencies in the early 1950's. Chemists from many areas of endeavor were required to solve problems posed by the large-scale industrial preparation of high-energy propellants. Proposed as attractive high-energy fuels were alkylated boron hydrides which, hopefully, were expected to perform substantially better than the hydrocarbons in use (1-7). It soon became obvious that the demands of this endeavor would involve a more exact examination of the underlying fundamentals. It was perhaps coincidental that the eventual fate of this research program followed a rather predictable course (8). While the borane fuels program did terminate, one of the more satisfying by-products was the discovery of an exciting new class of compound, carboranes, which show remarkable stability characteristics.

Because of the security shroud placed over these studies it is not yet clear exactly when and where the first work on the carboranes was performed and to whom the credit belongs. However, several sources (9) provide a degree of historical insight into this problem. Hopefully, a more clear account, if not a more lively one, will be forthcoming. It is interesting to note that as early as 1923 Stock and Kuss (10) were conducting experiments with carborane precursors, alkynes, and boron hydrides; however, they were not able to isolate and characterize the products.

The term carborane generally designates a carbon-boron-hydrogen system in which *both* the carbon and boron atoms are incorporated into a skeletal network. In comparison, the carbon atoms of compounds designated as organoboron hydrides are generally of a ligand nature. The use of the prefix "clovo" has been suggested for the closed polyhedral carboranes (e.g., Fig. 1) which, in addition, are named as derivatives of boron hydrides (11).

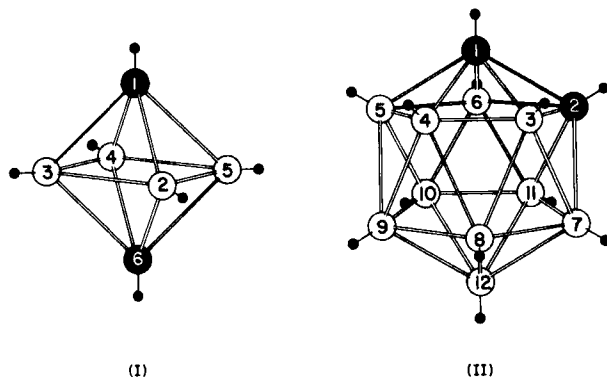


FIG. 1. Ball and stick models of 1,6-dicarbaclovohexaborane(6), (I), and 1,2-dicarbaclovododecaborane(12), (II). The latter compound is often abbreviated:



As in the past, the numerical suffix in parentheses indicates the number of hydrogen atoms in the parent compound (12, 13).

As is somewhat evident from the title, the general scope of this review is confined mainly to the chemistry of molecules containing $\text{H-B}_n\text{-C}$ groupings. Although several successful attempts to correlate the reactions and structures of the boron hydrides have been made (14-17), it is still

evident that much of the chemistry of each boron hydride is peculiar to itself. Therefore, the contents of this review are organized accordingly. There is no separate section devoted to the analytical problems that are sometimes encountered with C, B, H systems. However, analytical methods described elsewhere (18–21) provide for nearly all situations encountered.

In fairness to authors of work in which security restrictions have been lifted only recently, a rather unusual number of patents are cited. Until this work reaches the journal literature, it is not necessary to elaborate on the need to view some of the claims with a proportionate degree of reserve.

It is assumed that the reader has had some acquaintance with boron hydride chemistry and is somewhat familiar with the structures and bonding characteristics found in the well-known boron hydrides, e.g., diborane, tetraborane(10), pentaborane(9), pentaborane(11), and decaborane(14). For a recent review of the subject, a volume by Lipscomb (17) is highly recommended. In addition, surveys of related topics, as well as earlier reviews on the present subjects, are advised for completeness (7, 15, 16, 22–49).

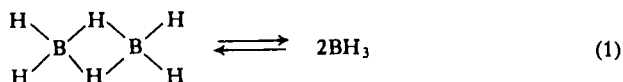
In this chapter ball and stick models are used from time to time to depict the skeletal structures of polyhedral boron hydrides. No attempt is made to portray these structures in terms of two- and three-center bonds since the author wishes to avoid the problems associated with the valence bond structural ellipsis (50, 51) implied even by a sophisticated representation (17).

II

ORGANO-SUBSTITUTED BORON HYDRIDES

A. Diborane and Borane Derivatives

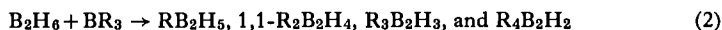
The readily established equilibrium,



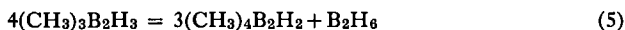
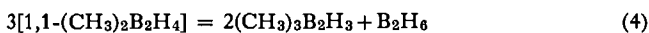
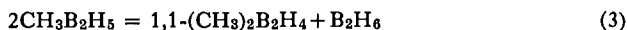
provides a compelling reason for including a discussion of both diborane and borane derivatives under the same general section of this review. Although the equilibrium normally lies far to the left for diborane and many of the organosubstituted diboranes, the presence of a sufficiently strong Lewis base leads to the formation of a monoboron adduct.

1. Preparation of Alkyl and Aryldiboranes

a. *Exchange between Diborane and Trialkyl and Triarylboranes.* Four of the five possible methyl- and ethyldiboranes can be prepared by the room temperature equilibration of diborane with the corresponding trialkylborane (52, 53).



Approximate equilibrium constants have been determined for the trimethylborane exchange from equilibration experiments (52) and from thermodynamic data (54).



Eq. no.	K_{expt}	K_{calc}
(3)	2.8	3.1
(4)	2.7×10^{-4}	5.2×10^{-4}
(5)	6.7×10^{-3}	3.5×10^{-3}
(6)	—	$\sim 10^{-12}$

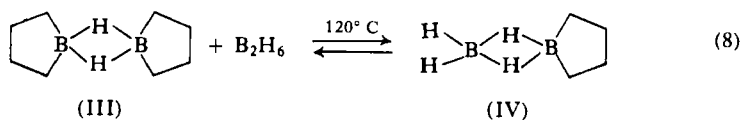
The alkylation follows pseudo-second-order kinetics ($k_f = 0.40 \pm 0.02$ liter min^{-1} mole $^{-1}$) after an induction period which is suppressed with an excess of diborane (55–57). From exchange studies carried out in ether solution (58–60) alkyl groups with large steric requirements were found to reduce the proportion of tetraalkyldiborane relative to the less alkylated products (59).

1,2-Dialkyldiborane, not detectably present in the above exchange, is obtained by the reversible disproportionation of the monoalkylated diborane (61, 62).



R	$K \times 10^2$	References
CH_3	7.01	56
C_2H_5	3.9 (g)	62
	16.9 (liq)	—

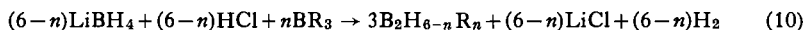
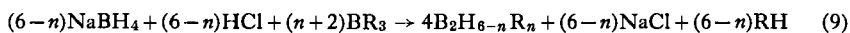
A related exchange involving a cyclic tetrasubstituted diborane (III) has been used to synthesize the corresponding asymmetrical derivative (IV) (63).



Historically, the discovery that not more than four of the six hydrogen atoms are replaced by alkyl groups provided chemical evidence in favor of the bridge model of diborane (57, 24). Thus far, no compound has been described in the literature in which an alkyl group bridges two boron atoms, as is observed in some related aluminum compounds, e.g., $\text{Al}_2(\text{CH}_3)_6$. However, a related bridging species may well be present as a high-energy intermediate during alkyl-boron exchange reactions (64).

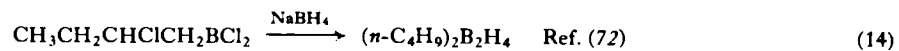
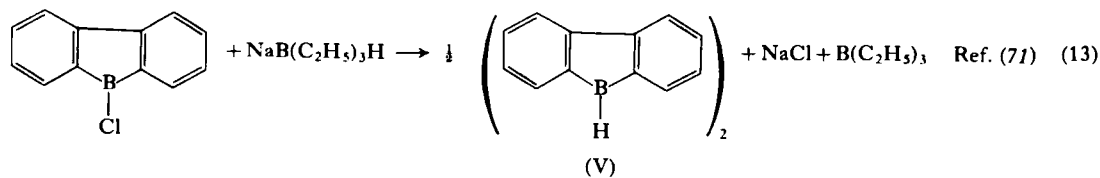
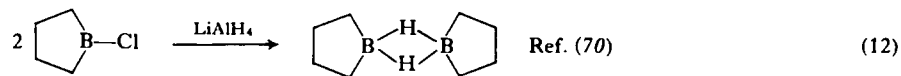
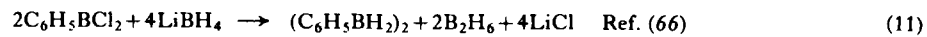
When a mixture of triphenylborane and diborane is heated to about 80°C in both the presence (65) and absence (66) of ether, 1,2-diphenyldiborane is the only phenyl-substituted diborane obtained. This is in striking contrast to the above alkyl exchange in which all diborane derivatives except the 1,2-dialkyldiborane are found.

b. *Reductions Involving the Use of Complex Metal Hydrides.* A mixture of a trialkylborane and hydrogen halide reacts at elevated temperatures under pressure with an inorganic complex hydride such as NaBH_4 , LiBH_4 , or LiAlH_4 to give a mixture of alkylated diboranes (67).

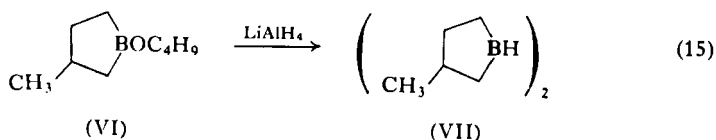


Alternatively, boron trichloride may be used in place of the hydrogen halide, or, the hydride may be treated with an alkylboron halide, R_2BX or RBX_2 (67, 68), or corresponding aluminum derivatives, AlR_3 , R_2AlX , RAlX_2 (69). As implied above [Eqs. (9) and (10)] the extent of diborane alkylation is controlled by the ratio of reactants. It is interesting to note that not only does the reaction proceed more readily with LiBH_4 than with NaBH_4 but it also follows a slightly different course. The former hydride releases no hydrocarbon, hydrogen being the only gas formed, whereas the reverse is observed with NaBH_4 (67).

Other reported reductions of alkyl or arylboron halides with ether solutions of complex metal hydrides imply a convenient general route to the 1,2-di- or tetrasubstituted diboranes.

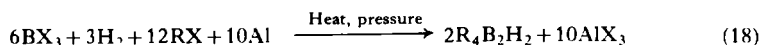
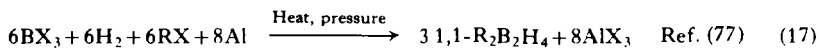
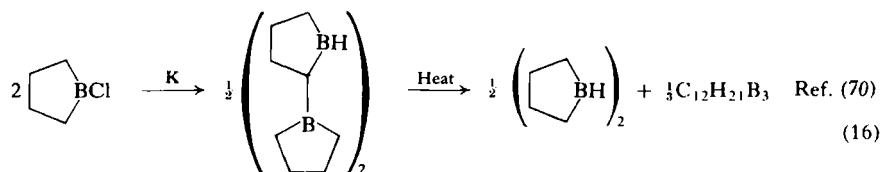


When the reduction of phenylboron dichloride is carried out with lithium aluminum hydride at the reflux temperature of dioxane (100° C) only the disproportionated products, triphenylborane and diborane, are found (73). In contrast, a similar reduction of diethylphenylboronate in diethyl ether at room temperature gives the phenylborane (dimer) which is isolated as the pyridine adduct (74). Also, 1-butoxy-3-methylboracyclopentane (VI) is reduced without difficulty by lithium aluminum hydride in ether solution to the corresponding tetrasubstituted diborane (VII) (75).

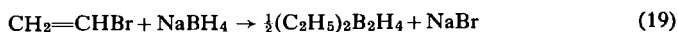


A reduction of trimethylboroxine with sodium borohydride reportedly gives methyldiboranes. However, no yield is recorded (76).

A few reductions involving metals have led to useful routes for preparing alkylated diboranes.



Perhaps one of the more promising one-step preparations deserving further study is the room temperature reduction of olefinic halides with NaBH_4 in diglyme (78, 79). The dialkylated diborane product from this reaction has been identified as the 1,1-isomer (80). This suggests rapid



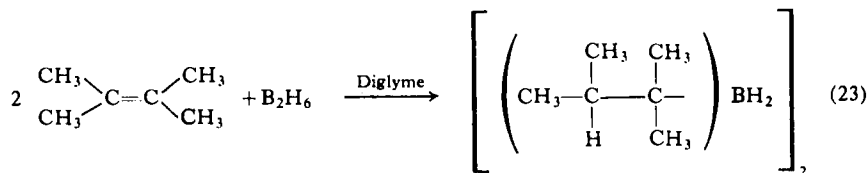
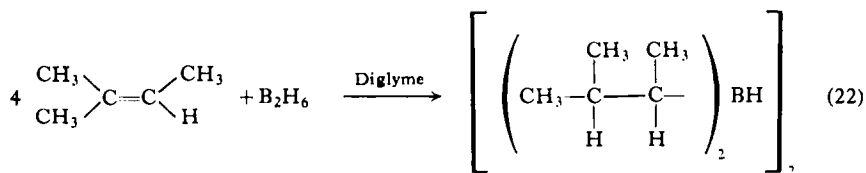
formation of trialkylboranes followed by an alkyl exchange as discussed in the previous section.

c. *Reduction of Organoboron Esters and Halides with Diborane.* The interaction of diborane and esters of dialkylborinic acids at room temperature yields predominately tetraalkyldiboranes, 1,1-dialkyldiboranes, and esters of alkylboronic acids (81, 82). If the reaction mixture is allowed to stand for one week, the unsymmetrical dialkyldiborane isomerizes into the symmetrical 1,2-derivative (82). Similar attempts to reduce diphenylboron chloride (65) and esters of diarylboronic or arylboronic acid (65, 83, 84) with diborane all result in formation of the 1,2-diaryldiborane.



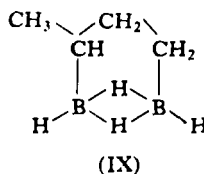
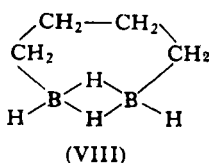
The absence of diphenylborane (as either dimer or 1,1-dipenyldiborane) in the product mixture is attributed to a disproportionation, which must be more rapid than with the corresponding alkyl compounds, to give the 1,2-diaryldiborane and triphenylborane. Undoubtedly, the latter compound reacts further with diborane under these conditions to form more of the observed product (Section II, A, 1, a).

d. *Hydroboration.* Hydroboration of the great majority of olefins with diborane at elevated temperatures (85) or at ambient temperatures in the presence of ethers (86, 87, 28) is usually allowed to proceed to the corresponding trialkylborane. However, it was quickly recognized that alkyl-diboranes are obvious intermediates in this reaction (88). In fact, equilibrium concentrations of the various alkylated diboranes are found when low ratios of olefin/diborane are used (58, 59). Further, when sterically hindered olefins are used, the reaction is conveniently stopped at the di- or tetraalkyldiborane stage. As a general rule, trisubstituted olefins, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, usually proceed to the tetraalkyldiborane,

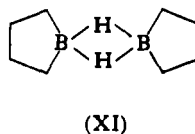


whereas, tetrasubstituted olefins, such as 2,3-dimethyl-2-butene, proceed only to the 1,2-dialkyldiborane stage (87, 89-96). This rule is, of course, subject to modification when extraordinarily large groups are attached to the double bond. For instance, *trans*-di-*tert*-butylethylene stops at the dialkyldiborane stage (97).

A vapor-phase reaction between butadiene and diborane at 100° C with hydrogen as a diluent produces, in addition to polymeric materials, an appreciable yield of the cyclic 1,2-tetramethylenediborane (VIII) and a smaller amount of 1,2-(1'-methyltrimethylene)diborane (IX) (98).



A similar cyclic structure (X) has been suggested (28, 94, 99) for the 2:1 butadiene-diborane product which was originally proposed to be bis(boracyclopentane) (XI) (100).

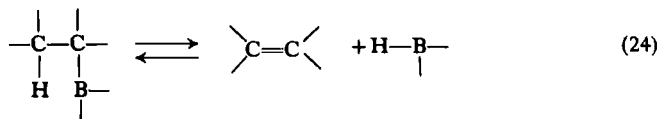


However, recent studies (63) support the earlier assignment (XI).

Only a minimum of mechanistic attention has been paid to the catalytic effect that ethers have on the hydroboration reaction. After determining that the hydroboration of olefins with 1,2-bis(3-methyl-2-butyl)diborane is first order in olefin and also first order in the substituted diborane, it was suggested that the role of the solvent is to coordinate with the dialkylborane monomer, the "leaving group" in this particular reaction (101). However, the room temperature hydroboration of ethylene with borine carbonyl (102) intimates, by analogy, that a rather loosely held adduct may account for acceleration of B—H addition to unsaturated systems in ether solvents. The use of a molybdena-aluminum catalyst has been moderately effective in converting an ethylene-diborane mixture to a mixture of ethyldiboranes at room temperature (103).

There is indirect evidence that $\text{H}_2\text{BCH}_2\text{CH}_2\text{BH}_2$ is formed from acetylene and excess diborane in the presence of 1,2-dimethoxyethane (103a).

e. *Dehydroboration*. The reversibility of the hydroboration reaction was first realized when dibutyldiborane and olefin were obtained from tri-*n*-butylborane at elevated temperatures (104).



Other dehydroboration reactions have since been observed (105–107), and have occasionally even been used to synthesize alkylated diboranes (36, 108, 109). As with hydroboration, dehydroboration is catalyzed by ethers (92, 110). Thus, in diglyme solution a marked enhancement of organoborane isomerization is observed (110, 111)¹; and tetraisopinocamphenyldiborane appears to be in equilibrium with substantial amounts of triisopinocamphenyldiborane and α -pinene (92, 93).

A dehydroboration–hydroboration sequence is probably operating when thermal action converts seven- or eight-membered rings of bis(boracycloalkanes) into the more stable six-membered ring (100, 112).

f. *Other Methods of Preparation*. Included in this section are reactions that are not conveniently covered in the preceding sections and have not been widely used in the synthesis of alkyl or aryl diboranes.

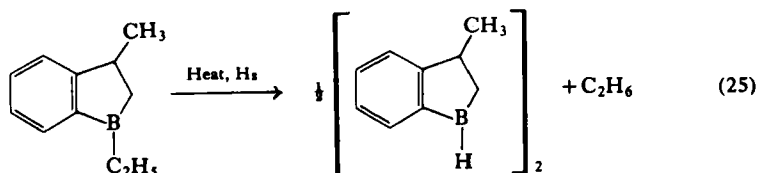
Alkylated diboranes are produced by exchange of diborane with a few metal alkyls, e.g., ethyllithium (113) and trimethylgallium (114). Similarly, alkyl exchange has been observed between aluminum borohydride and both tin and lead tetramethyl with formation of, among other products, methylated diboranes (115).

A reported preparation of phenylborane (dimer) from a reduction of $\text{C}_6\text{H}_5\text{BI}_2 \cdot 2\text{HI}$ with hydrogen in ethanol (116) is undoubtedly in error (66, 73). Perhaps the first unquestionable evidence for the existence of this compound comes from the reaction of diborane with benzene at elevated temperatures (85).

Hydrogenation of a trialkylboron, used occasionally to prepare tetraalkyldiboranes (117–119), probably occurs through direct addition to the

¹ The isomerization may not necessarily (111a) involve an elimination-addition mechanism (111b).

carbon-boron bond (120, 121) rather than a dehydroboration followed by hydrogenation of the resulting olefin.

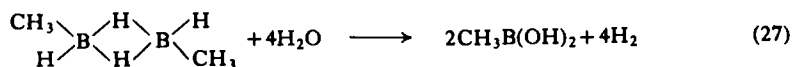
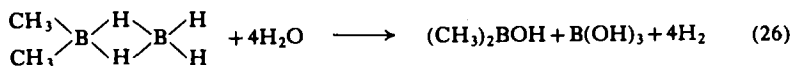


Dialkylaluminum hydrides reportedly enter into an exchange reaction with borate esters (122) or trialkylboroxines (123) to give about 40% yields of tetraalkyldiboranes.

A mixture of *n*-propyldiboranes is obtained along with tri-*n*-propylborane from the reaction of diborane with cyclopropane at about 95°C. Apparently the "banana" bonds of cyclopropane can provide sufficient electron density to form the expected pi-complex intermediate (124).

2. Reactions of Alkyl and Aryldiboranes

a. *Hydrolysis, Alcoholysis, and Related Reactions.* As with diborane, the bridge and terminal boron-bonded hydrogens of alkylated diboranes are normally quite labile at room temperature toward hydrolysis and alcoholysis (28, 52, 53, 58-62, 78, 79). Since the alkyl-boron bonds are not usually cleaved, the alkylboronic or alkylborinic acids (or esters in the case of alcoholysis) produced are often quite useful in determining the structure of the original alkylated diborane. Similarly, dialkylthioborinic esters are



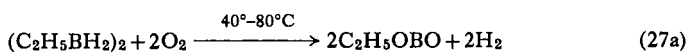
obtained from the interaction of tetraalkyldiboranes with thiols (125, 60). 1,2-Diaryldiboranes react with hydroxy compounds in a manner analogous to the 1,2-dialkyldiboranes (66, 83, 85, 126).

A notable exception to the rather labile character of B—H bonds of alkyl-diboranes toward the reagents under discussion is bis (boracyclopentane)

(XI). This compound undergoes hydrolysis and alcoholysis only at elevated temperatures (about 100° C) (63, 100).

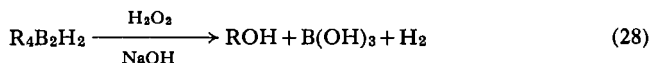
Reactions of alkyl and aryl diboranes with ammonia and amines are given in Section II, A, 2, f.

b. *Oxidation and Oxidative Hydrolysis.* As with diborane and trialkylboranes, alkyl derivatives of diborane react vigorously with air (43, 60), presumably with the formation of B—O and R—O bonds. In a study on the nonexplosive partial oxidation of 1,2-diethyldiborane the rate dependence was found to be zero order in oxygen and first to three-halves order in 1,2-diethyldiborane, with an activation energy of 32.5 ± 1.5 kcal/mole (127).



Tetramethyldiborane, 1,1-dimethyldiborane, and diborane are all much more stable than trimethylborane toward oxidation with molecular oxygen in the low temperature region of 77°–170° K. This work would tend to support a primary oxidation step involving formation of a coordinate bond between oxygen and the empty orbital of the boron atom. Diborane and its methyl derivatives do not possess energetically accessible vacant orbitals; and further, the heat of dissociation of the BH₂B bridging unit (Section II, A, 3) is sufficiently high to prevent dissociation and reactions of the monomeric borane species at the low temperatures studied (127a).

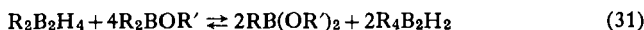
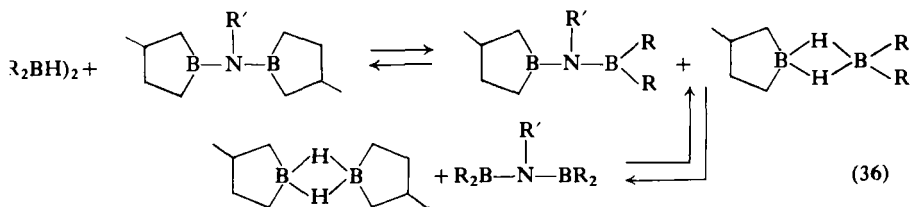
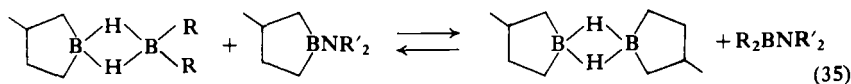
Oxidative hydrolysis with hydrogen peroxide has been used extensively in sequence with the hydroboration reaction in the synthesis of alcohols from olefins via alkylated diboranes (28).



c. *Disproportionation and Exchange Reactions.* The reversible nature of the alkyl exchange between trialkylboranes and diborane (Section II, A, 1, a) is implied in several studies (52, 56, 128). This disproportionation behavior may partially account for the production of trialkylboranes by the thermal interaction of diborane with olefins (85) after the initial formation of an alkyl diborane by an addition step (88). Alternatively, of course, the trialkylborane may arise solely through a series of B—H additions (88).

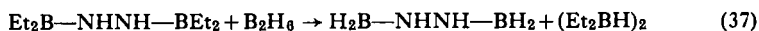
1,2-Diphenyldiborane appears to be moderately stable toward disproportionation at room temperature (66, 74, 83), although at 100° C in dioxane a reaction which should have yielded this phenyl derivative resulted instead in the formation of triphenylborane and diborane (73). All attempts to obtain

Dialkyl and tetraalkyldiboranes have been shown to equilibrate with boric, alkylboronic, and dialkylborinic esters as illustrated in Eqs. (29–31) (81, 82, 130).


$$2R_4B_2H_2 + NaOCH_3 = NaBH_4 + 2BR_3 + R_2B(OCH_3) \quad (32)$$
$$\text{BR}_3 + 2\text{B(OR')}_3 \xrightarrow[\text{(Cat. amt.)}]{\text{R}_4\text{B}_2\text{H}_2} 3\text{RB(OR')}_2 \quad (33)$$
$$(R_2BH)_2 + \text{cyclopentyl-BNR}'_2 \rightleftharpoons \text{cyclopentyl-B(H)-B(R)}_2 + R_2B\text{NR}'_2 \quad (34)$$


Studies on the disproportionation of methyl(dimethylamino)borane (137) would tend to support an exchange mechanism that does not involve breaking

of the B—N bond in the above bis(boracyclopentane) transformations. For the same reason B—N cleavage probably does not occur in a related exchange between diborane and hydrazino-1,2-bis(diethylborane) (138).

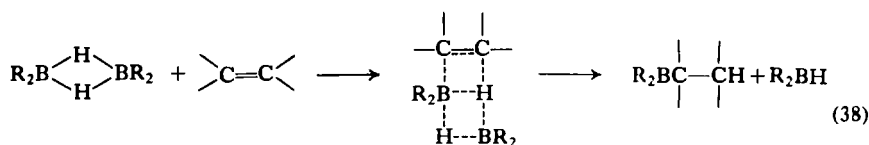


Exchange reactions of alkylated diboranes with higher boron hydrides are discussed in Sections II,B,1 and II,D.

d. *Hydroboration*. For an extensive discussion of the role of alkylated diboranes in the hydroboration reaction one is advised to consult the recent and authoritative book by H. C. Brown (28). This section will include only a brief summary of pertinent chemistry as well as inclusion of new literature.

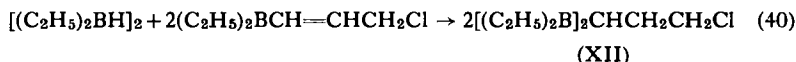
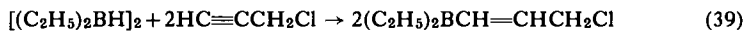
Alkylated diboranes with large steric requirements [e.g., 1,2-bis(2,3-dimethyl-2-butyl)diborane, tetra(3-methyl-2-butyl)diborane, and tetra-cyclohexyldiborane] are used extensively as selective reducing agents (28). Applications have included: (1) the competitive hydroboration of olefins and dienes (94, 95, 139–144); (2) additional steric control over the mode of addition to olefins and alkynes (94, 95, 139, 140, 144–146); (3) use as a monohydroborating agent of alkynes and dienes (94, 142, 145, 147, 148); (4) the selective reduction of various allyl derivatives (149–151); (5) the asymmetric synthesis of alcohols from the hydroboration of olefins with optically active alkylated diboranes (96, 144, 152–156). In addition, tetra(3-methyl-2-butyl)diborane has found use as a reagent for the steric control of the reduction of several cyclanones to alcohols (157), and for selective hydroborations in the presence of unprotected carboxylic groups (158).

A comparison of relative hydroboration rates of olefins with tetra(3-methyl-2-butyl)diborane indicates the following general order: alkynes > terminal olefins > *cis* internal olefins > *trans* internal olefins (143). Kinetic data establish the hydroboration of olefins with this tetraalkyldiborane to be second order, first order in olefin, and first order in the substituted diborane (101). Presumably, the rate-determining step gives, in addition to the trialkylborane product, one molecule of a dialkylborane monomer which may dimerize or react with a second molecule of olefin in a rapid second step. Since the dialkylborane dimer rather than monomer participates in the

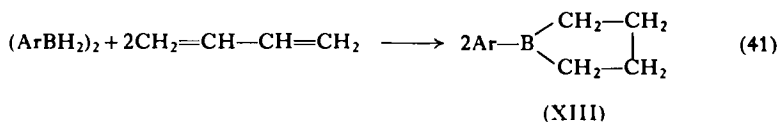


activated complex, it is not surprising that fairly selective hydroborations are observed with tetraethyldiborane (133).

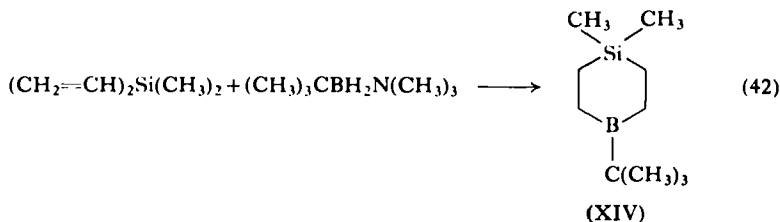
A stepwise reduction of the triple bond of propargyl chloride with tetraethyldiborane is observed with the formation of 1,1-bis(diethylboryl)-3-chloropropane (XII) (159).



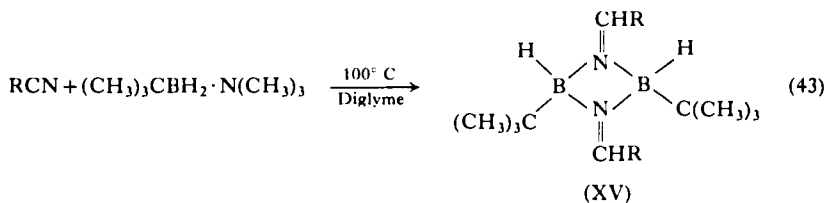
Unsymmetrical trialkylboranes are isolated by hydroboration of alkenes with tetraalkyldiboranes (60–60b). In contrast, phenyldialkylboranes, prepared from 1,2-diphenyldiborane, undergo a rapid redistribution at room temperature into triphenylboron and a trialkylboron (126). 1,2-Diaryl-diboranes add to 1,3-dienes in toluene with the formation of 1-arylboracyclopentanes (XIII), which appear to be more stable toward disproportionation than the open chain analogs (126).



Hydroboration of olefins with trimethylamine-*tert*-butylboranes provides an alternative route to unsymmetrical trialkylboranes. An interesting application of this reaction is the synthesis of 1-bora-1-*tert*-butyl-4,4-dimethyl-4-silacyclohexane (XIV) (160, 161).

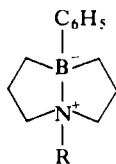


Trimethylamine-*tert*-butylborane has also been used successfully in reactions with terminal alkynes (161) and nitriles (162), affording *tert*-butyldi(1-alkenyl)boranes and dimeric alkylideneamine-*tert*-butylboranes (XV), respectively.

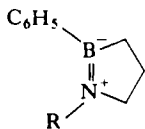


Other derivatives of (XV) have been prepared by adding tetraalkyldiboranes to acetonitrile (80).

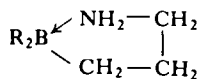
The reduction of diallyl alkylamines with triethylaminephenylborane results in two products, a stable solid and an air-sensitive liquid, to which structures (XVa) and (XVb) have been assigned, respectively (162a). When allylamine is added to an ether solution of a tetraalkyldiborane the predominant product is the inner complex (XVc) (162b).



(XVa)



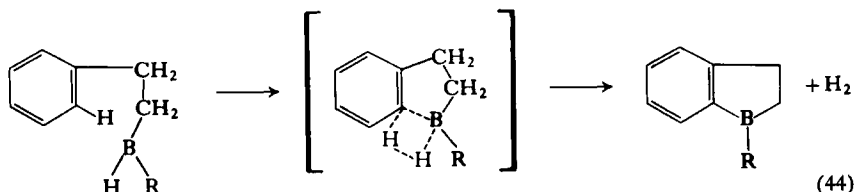
(XVb)



(XVc)

The formation of heterocyclic organoboranes from alkenes and alkylated diboranes has been recently reviewed (22b).

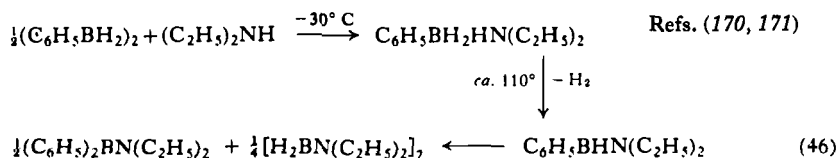
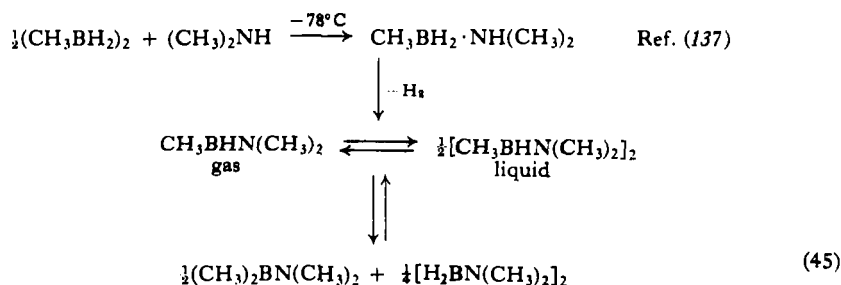
e. *Reactions with C—H to Give C—B Bonds.* Tetraethyldiborane reacts with benzene at about 200° C to produce triphenylborane in 25% yield (163). Similar reactions have been effected intramolecularly in the syntheses of boron heterocycles (97, 108, 119, 164, 165), and probably occur through a concerted four-center transition state mechanism (36).



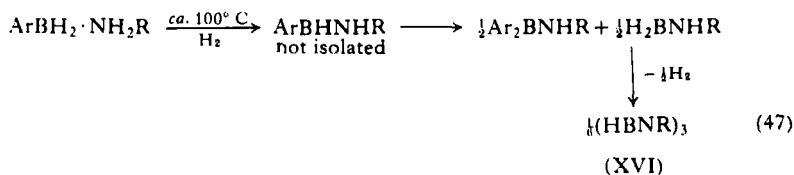
f. *Coordination Compounds with Lewis Bases.* The behavior of methylated diboranes toward ammonia at low temperatures is similar to diborane in that white saltlike "diammoniates" are formed (61, 166, 167). This suggests that the methylated derivatives are substituted bis(ammonia)boronium

borohydrides (168, 169) which, if correct, poses an interesting substituent-placement question. Although the stability of the adducts decreases with increasing number of methyl groups, there appears to be no disproportionation of one into the others. Dimethylaminoborane is produced by the mild decomposition of the diammoniates of 1,1-dimethyl-, trimethyl-, and tetramethyldiboranes whereas heating the diammoniates to 200°C in a closed tube affords *B*-methyl derivatives of borazine (61, 166).

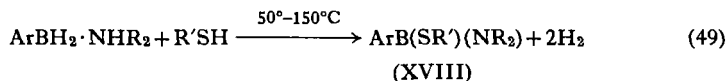
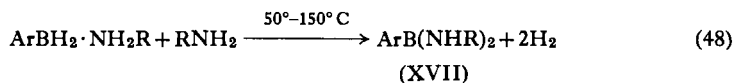
Primary and secondary amines react with 1,2-alkyl or aryldiboranes to give amine-borane adducts which, with appropriate thermal encouragement, evolve hydrogen and yield the corresponding aminoboranes. Aminoboranes generally exhibit a tendency to disproportionate by reversibly exchanging R (or Ar) for H on boron.



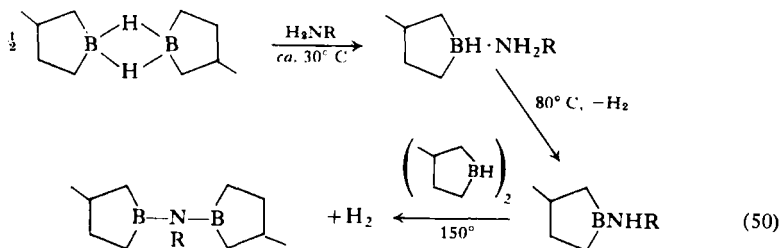
The complexes of 1,2-diaryldiboranes with primary amines behave analogously when heated, the only difference being that the alkylaminoboranes formed from the symmetrization step are further converted to *N*-trialkylborazines (XVI) (84).



On heating the complexes in the presence of excess amine, or with thiols, high yields of bis(alkylamino)arylborines (XVII) (84) or (alkylthio)(dialkyl-amino)arylborines (XVIII) (171), respectively, are obtained.

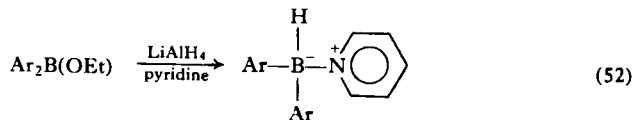
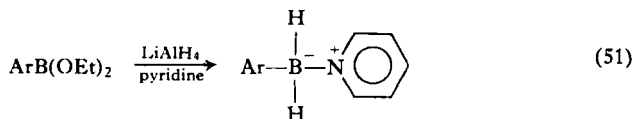


Similar chemistry is observed with the primary amine complexes of dialkylboranes (60, 63).



The reactions of 1,2-diphenyldiborane with alkyl (and aryl) diamino-boranes (171a) and with diamines (171b) have been investigated.

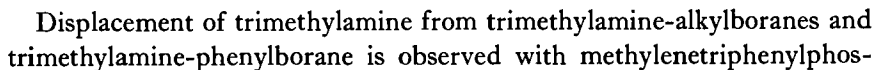
A general method of obtaining tertiary amine or pyridine complexes of organo-substituted boranes has been developed (172) which avoids the previous necessity of preparing intermediate alkylated diboranes in a separate step (61, 66). This relatively new route involves reduction of an appropriately substituted boronate or borinate (or boroxine) with lithium aluminum hydride in the presence of the desired amine (66, 74, 129, 173, 174).



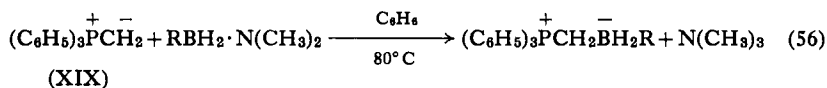
The hydrolysis of pyridine-diphenylborane follows second-order kinetics, first-order both in water and amine-borane (175). An observed kinetic isotope effect is small and temperature-independent for substitution of deuterium for protium on boron, whereas, the effect is large and temperature-dependent for a similar isotopic substitution in water (175, 176). A mechanism consistent with the isotope effect involves an initial attack of water on the boron-hydrogen bond



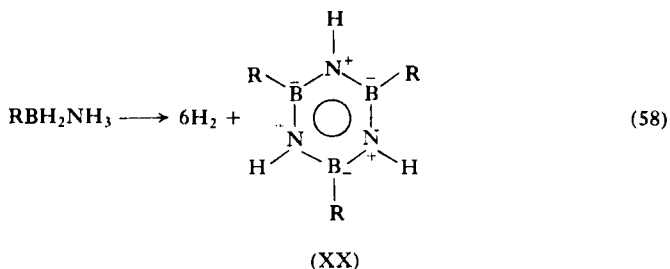
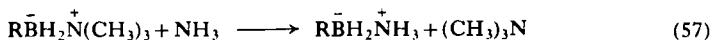
Trimethylamine-alkylboranes react with two equivalents of alkanethiols at 60°-100°C, affording the corresponding dialkyl alkylthioboronate esters (178).



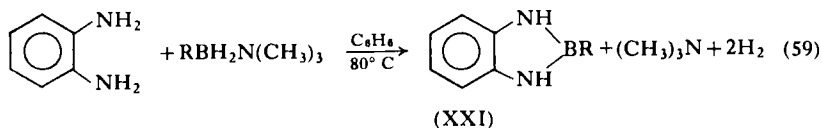
phorane (XIX). The qualitative order of reactivity, $R = \textit{tert}$ -butyl > 2-butyl > methyl, suggests that these reactions occur by the combination of the free



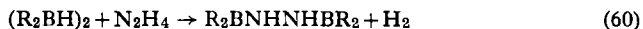
borane and substrate (179). Both first- and second-order kinetic terms have been determined for the displacement of trimethylamine from trimethylamine-alkyl- and arylboranes with tri-*n*-butylphosphine (179a). In an ammonium chloride-catalyzed reaction between trimethylamine-alkylborane and ammonia at 100°–150° C, formation of the observed product, *B,B,B*-trialkylborazine (XX) (180, 181), is probably preceded by a displacement reaction [Eq. (57)].



In a similar fashion *o*-phenylenediamine reacts with trimethylamine-alkylboranes with eventual loss of trimethylamine and hydrogen, and the formation of 2-alkylborabenzimidazolines (XXI) (173).

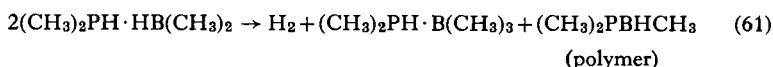


The action of tetraalkyldiboranes on hydrazine at 100°–150° C affords *B*-substituted hydrazinoboranes in good yield (182).

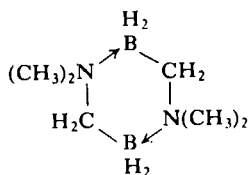


Dimethylphosphine-dimethylborane prepared from dimethylphosphine and tetramethyldiborane, undergoes disproportionation above 40° C, and

upon heating to 165° C there is some evidence that the main reaction is (183)



A ring compound with a repeating BCN sequence (XXIa) is obtained in low yield from sodium hydride and $\text{H}_2\text{B}[\text{N}(\text{CH}_3)_3]_2^+ \text{Cl}^-$ (183a).



3. Diborane-Borane Equilibrium

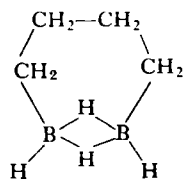
All mono- and dialkylboranes are known as dimeric species in which each boron is tetracoordinated and bonded to the adjacent boron through two bridge hydrogens (52) (Table I, 184, *etc.*). Apparently, the presence of large bulky alkyl groups such as 3-methyl-2-butyl does not lead to any observable dissociation even in the tetraalkyldiboranes (92). Moreover, there is no indication that alkylated diboranes are dissociated in tetrahydrofuran (92), a solvent which readily dissociates diborane itself (185, 186). Steric influences may be responsible for the instability of the alkylborane addition compounds relative to those formed by borane. Moreover, the bridge structures in the alkyl-substituted diboranes might be expected, on the basis of compensating polar effects (92), to possess stabilities comparable to that of diborane.

Over 10 years ago an interesting observation was made to the effect that bridge bonding occurs only when the hydrogen atoms have a partial negative charge (187). On the basis of the performed calculations a number of known compounds, including alkylated diboranes, fitted well within this scheme. However, the hydrogen atoms of both phenylborane and diphenylborane were given positive charges which implied predominately monomer character for these compounds. Since then, phenylborane has been synthesized and found to occur as a dimer (66, 83), and a diarylborane, 9-borafluorene (V), has been reported to exist as a colorless dimer which, however, dissociates into the yellow monomer when a benzene solution is heated to 80° C (71).

TABLE I
ALKYL AND ARYLDIBORANES

Compound	Physical properties			References
	B.p. (° C)/mm)	M.p. (° C)	Other ^a	
CH ₃ B ₂ H ₅	<i>ca.</i> -78.5°/55	—	—	52
1,2-(CH ₃) ₂ B ₂ H ₄	-78°/7	-124.9°	$\log P = 7.523 - (1290/T)$	61
1,1-(CH ₃) ₂ B ₂ H ₄	-78.5°/10	-150.2°	$\log P = 7.363 - (1212/T)$	52
(CH ₃) ₃ B ₂ H ₃	45.5°	-122.9°	$\log P = 7.673 - (1527/T)$	52, 118
(CH ₃) ₄ B ₂ H ₂	68.6°	-72.5°	$\log P = 7.687 - (1643/T)$ Raman (184)	52, 67, 118
C ₂ H ₅ B ₂ H ₅	-78.5°/7	—	—	53
1,2-(C ₂ H ₅) ₂ B ₂ H ₄	0°/36	—	IR	62
1,1-(C ₂ H ₅) ₂ B ₂ H ₄	0°/42	—	$\log P = 8.055 - (1760/T)$	53
	0°/46	—	IR	62
(C ₂ H ₅) ₃ B ₂ H ₃	109°-111°	—	—	118
	0°/4	—	—	53
(C ₂ H ₅) ₄ B ₂ H ₂	0°/5	—	—	53, 118
<i>n</i> -C ₃ H ₇ B ₂ H ₅	-60°/6.2	—	—	53
1,1-(<i>n</i> -C ₃ H ₇) ₂ B ₂ H ₄	33-34°/32	—	n_D^{20} 1.4088	60
	0°/2.8	—	—	53
(<i>n</i> -C ₃ H ₇) ₄ B ₂ H ₂	76°/21	—	H ¹ NMR (68) n_D^{20} 1.4327 $d_4^{20} = 0.7388$ (60)	60, 67
		—	n_D^{20} 1.4375 $d_4^{20} = 0.7647$ (60)	118
(<i>n</i> -C ₄ H ₉) ₄ B ₂ H ₂	98°/12	—	—	60
	40-41°/0.25	—	IR (p. 186, ref. 28)	92
1,2-[CH(CH ₃) ₂ C(CH ₃) ₂] ₂ B ₂ H ₄	-34.7° to -32.3°	—	IR (p. 184, ref. 28)	92
1,1-[CH(CH ₃) ₂ CH(CH ₃)] ₂ B ₂ H ₄	—	—	IR (p. 182, ref 28)	92
[CH(CH ₃) ₂ CH(CH ₃)] ₄ B ₂ H ₂	—	<i>ca.</i> 40-44°	—	92

(Cyclohexyl) ₄ B ₂ H ₂	—	102°–106°	—	118
		103°–105°		92
(<i>trans</i> -2-Methylcyclohexyl) ₄ B ₂ H ₂	—	116°–119°	—	92
(Isopinocampheyl) ₄ B ₂ H ₂	—	—	[α] _D ²⁰ = −37.1°	92
1,2-(C ₆ H ₅) ₂ B ₂ H ₄	—	82°–85°	—	65
		85°		66
		81°–83°		83
1,2-(<i>p</i> -CH ₃ C ₆ H ₅) ₂ B ₂ H ₄	—	128–132°	—	84
		(dec.)		
1,2-(<i>p</i> -ClC ₆ H ₅) ₂ B ₂ H ₄	—	115°–117°	—	83
1,2-(α-C ₁₀ H ₇) ₂ B ₂ H ₄	—	117°–119°	—	83

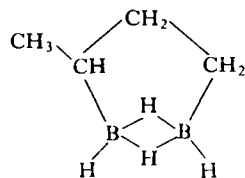


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MS, B¹¹ and H¹ NMR, IR

98



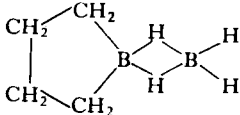
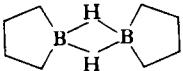
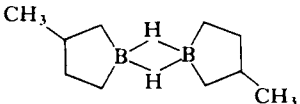
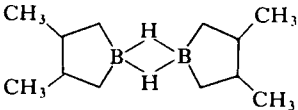
0°/39

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MS, IR

98

TABLE I—*continued*

Compound	Physical properties			References
	B.p. (°C/mm)	M.p. (°C)	Other ^a	
	—	—	IR	63
	76°–77°/10 (63)	—	IR, n_D^{20} 1.4894, d_4^{20} 0.8541 (63)	100
 (Mixture of isomers)	95°/12 37°/1	—	IR (63)	100 75
 (Mixture of isomers)	120°–124°/12	—	n_D^{25} 1.4683	63

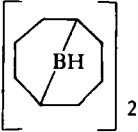
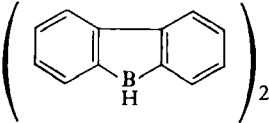
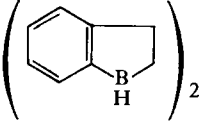
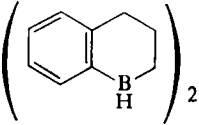
	—	142°	—	100
 Bis(borafluorene)	—	107°	—	71
 Bis(boraindane)	—	132°	—	118, 119
 Bis(boratetralin)	—	103–104°	—	118, 119

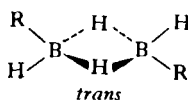
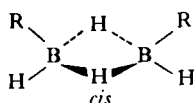
TABLE I—continued

Compound	Physical properties			References
	B.p. (° C/mm)	M.p. (° C)	Other ^a	
<p>The structure shows a benzene ring fused to a five-membered ring containing a boron atom (B) and a hydrogen atom (H). A methyl group (CH₃) is attached to the 3-position of the five-membered ring. The entire structure is enclosed in large parentheses with a subscript 2, indicating a dimeric compound.</p> <p>Bis(3-methylboraindane)</p>	—	119°	—	119

^a In this table *P* = pressure; IR = infrared; MS = mass spectrum; NMR = nuclear magnetic resonance. The references for the infrared spectra of the first ten compounds are given in Section II, A, 4.

The bridge-breaking energies for the various methyldiboranes have been estimated to fall in the 25–28.5 kcal range (54); however, these figures may have to be revised upward by about 4–10 kcal (188).

The only alkyldiborane capable of geometrical isomerism is the 1,2-dialkyldiborane. Of the two possible forms the *trans* configuration should predominate under equilibrium conditions on steric grounds. However, this has not received experimental verification.



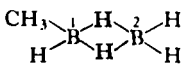
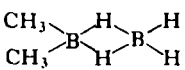
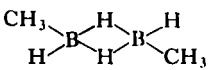
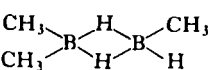
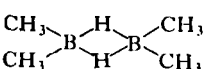
4. B^{11} NMR, Infrared, and Mass Spectra of Alkyldiboranes

The B^{11} NMR chemical shifts (Table II) of the methylated diboranes exhibit two major trends (128). First, alkyl groups tend to shift the resonance absorption of attached boron nuclei to lower field (about 4 ppm per alkyl group). Second, unsymmetrical substitution promotes a more pronounced shift to lower field for the more substituted boron, as well as a shift to higher field for the less substituted boron. Quantitatively, about 6 ppm is added or subtracted when the two parts of the molecule differ by one alkyl group; this value is doubled to about 12 ppm for a difference of two alkyl groups.

From rather extensive studies on alkylated diboranes in the infrared region of the spectrum characteristic features have been assigned for the various B-isomers (Table II, 189) (190–200). Those that contain a terminal BH_2 group (i.e., mono- and 1,1-dialkyldiboranes) exhibit twin peaks in the region of 2500 cm^{-1} , whereas the isomers with only terminal B—H groups (1,2-dialkyldiborane, trialkyldiborane) exhibit singlets. The tetraalkyldiboranes, of course, exhibit no terminal B—H stretching frequency. The BH_2 stretching frequencies are lowered by about $10\text{--}15\text{ cm}^{-1}$ for each alkyl group substituted on the other side of the bridge and lowered by about 25 cm^{-1} by an alkyl group attached to the same side. An intense band assigned to the asymmetric in-phase stretching of the BH_2B bridge is located in the $1580\text{--}1610\text{ cm}^{-1}$ region of all alkyldiboranes, except 1,1-dialkyldiboranes, where it is characteristically lowered by about 50 cm^{-1} . This general rule is not applicable to strained cyclic systems (98).

The mass spectra of isotopically labeled methyl- and ethyldiboranes have been studied (201, 202).

TABLE II
B¹¹ NMR AND INFRARED ASSIGNMENTS FOR METHYLATED DIBORANES

Compound	B ¹¹ NMR ^a			Selected infrared frequencies ^b	
	δ	$\mathcal{J}_T(\text{cps})$	$\mathcal{J}_B(\text{cps})$	B—H _T stretch (cm ⁻¹)	Asym in-phase B—H _B stretch (cm ⁻¹)
	B(1) —26.7	127 ± 5	41 ± 6	sym 2513	1592
	B(2) —8.8	127 ± 5	48 ± 5	asym 2571	
	B(1) —36.4	—	36.4	sym 2494	1546
	B(2) —3.6	125.5	49.7	asym 2571	
 and/or <i>cis</i> isomer	—20.5	131.2	47.5	2519	1610
	B(1) —29.2	—	38.9	2506	1605
	B(2) —13.6	133.7	45.2		
	—24.8	—	39.7	—	1605

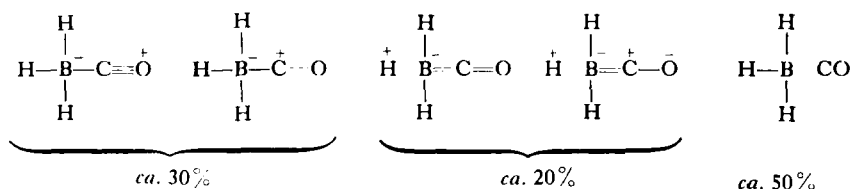
^a Chemical shift in ppm relative to boron trifluoride etherate (189). For comparison: diborane $\delta = -16.6$; $\mathcal{J}_T = 128 \pm 4$, $\mathcal{J}_B = 48$; B(CH₃)₃, $\delta = -84$; \mathcal{J}_T is the boron-terminal hydrogen coupling constant; \mathcal{J}_B , the boron-bridge hydrogen coupling constant.

^b H_T, terminal hydrogen atom; H_B, bridge hydrogen atom.

5. Carbon Monoxide-(C—B)Borane; BH₃CO

The unstable compound carbon monoxide-(C—B)borane (12), BH₃CO, prepared from diborane and carbon monoxide under elevated pressures (203), has been the subject of intensive spectroscopic investigations. Electron diffraction measurements (204) indicate that the molecule has its B—C—O

atoms linearly arranged with the three hydrogens attached to the boron, giving over-all C_{3v} symmetry. Microwave studies (205–207) have confirmed this structure and, in addition, provided more precise values for the molecular dimensions ($d_{BH} = 1.194 \text{ \AA}$, $d_{BC} = 1.540 \text{ \AA}$, $d_{CO} = 1.131 \text{ \AA}$, angle $HBH = 113^\circ 52'$). To explain the nature of the bonding in BH_3CO the following resonance contributions have been suggested (204, 207, 208) and weighted (207) on the basis of the microwave data and dipole moment measurements (209).

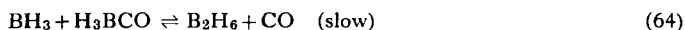
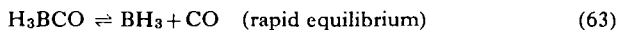


Additionally, the ionic character of the BC bond has been estimated to be about 20 to 30% (210) from the observed quadrupole coupling constant of B^{11} (205). Infrared (200, 211–214) and Raman spectra (211, 215, 216) results for BH_3CO are in essential agreement with the assigned structure. Using available spectroscopic data, potential energy constants, rotational distortion constants, and thermodynamic properties have been calculated for BH_3CO (211, 213, 217–219).

Decomposition of BH_3CO occurs readily at room temperature, although



equilibrium is not reached in a short time unless the mixture is heated to 100°C (203). The rapid decrease in rate at the initial stage of the reaction is attributed to an inhibitory effect of carbon monoxide. The other product, diborane, has no appreciable effect upon the rate in the early stages of decomposition. From a kinetic study a mechanism has been proposed in

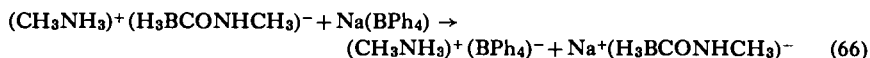
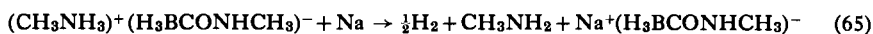


which the rate-limiting step is the displacement of carbon monoxide by a borane fragment [Eq. (64)] (220). This mechanism was challenged (221–223), but has recently been vindicated (188).

The products isolated from the reaction of carbon monoxide with alkylated diboranes do not contain the B—H bonds expected of a partially alkylated

BH_3CO (224). It is suspected (31, 43, 102) that these compounds contain $(\text{BCO})_2$ hexatomic rings similar to the rearranged products obtained from trialkylborons and carbon monoxide (225, 226).

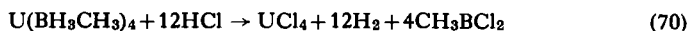
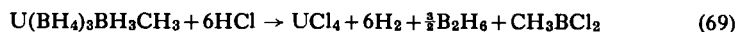
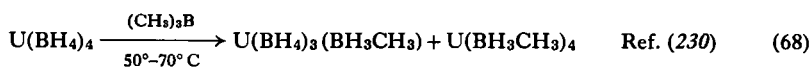
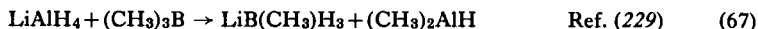
In a reaction with trimethylamine, BH_3CO merely loses carbon monoxide with the simultaneous formation of trimethylamine-borane (203). However, with ammonia a solid material stable at room temperature is formed, with the formula $\text{BH}_3\text{CO}(\text{NH}_3)_2$. Monomethylamine reacts with BH_3CO in the same manner as ammonia, forming a compound of the composition $\text{H}_3\text{BCO} \cdot 2\text{NH}_2\text{CH}_3$ which is moderately stable toward air and water. Using X-ray diffraction the structure of this adduct has been established as $[\text{CH}_3\text{NH}_3]^+[\text{H}_3\text{BCONHCH}_3]^-$. Analogous structures are implied for the ammonia and dimethylamine adducts. The compound $\text{H}_3\text{BCO} \cdot 2\text{NH}_2\text{CH}_3$ reacts with sodium in liquid ammonia and with sodium tetraphenylboron (227).

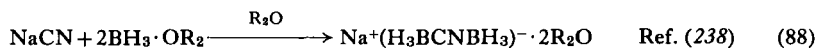
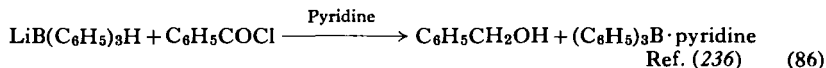
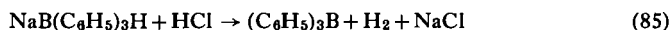
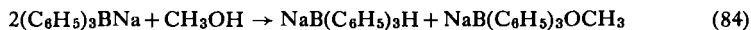
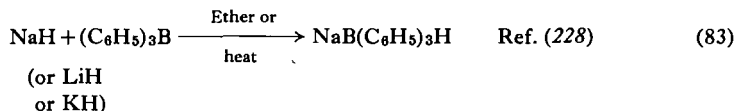
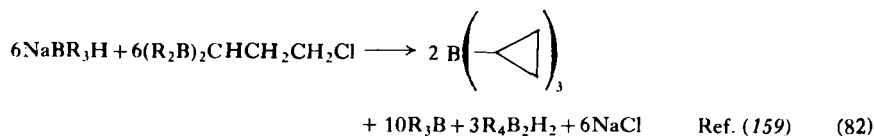
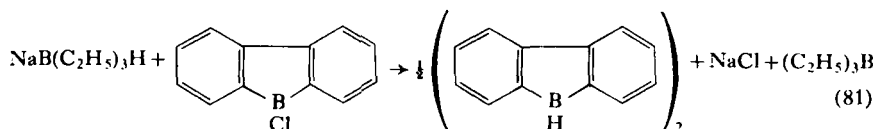
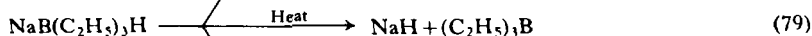
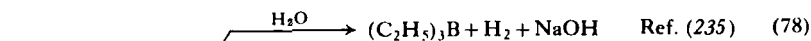
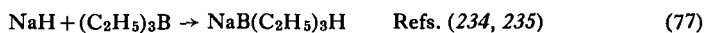
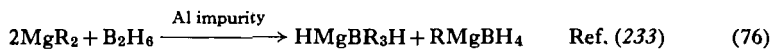
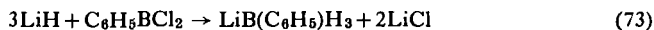
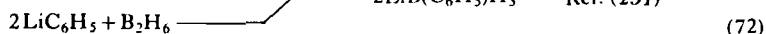


In a reaction reminiscent of the ether-catalyzed hydroboration reaction (Sections II,A,1,d and II,A,2,d), the B—H bonds of BH_3CO add to ethylene at ambient temperatures to form triethylboron with the release of carbon monoxide (102).

6. Metal and Ammonium Organotetrahydroborates

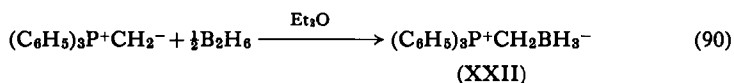
The first organo-substituted tetrahydroborate to appear in the literature was $\text{M}^+[\text{BH}(\text{C}_6\text{H}_5)_3]^-$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$), obtained by addition of triphenylborane to an alkali-metal hydride. Alternatively, the sodium derivative was prepared by the methanolysis of sodium triphenylborane (228). Since then, many other organotetrahydroborates have been prepared and some of their chemical reactions studied. These are summarized in Eqs. (67)–(89).



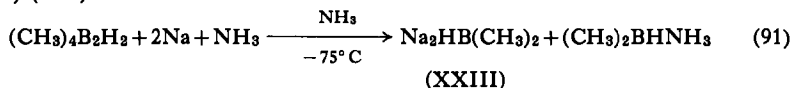


Although it is convenient to think of these compounds as organic analogs of metal tetrahydroborates, it is somewhat surprising to find the B—H infrared band for the triethyl derivative at $5.4\ \mu$, a region generally attributed to bridge bonds (235). A bridge bond may also account for the observed B^{11} NMR spectra (128). An infrared spectrum of the methyl derivative of lithium borohydride also indicates a considerable change in structure relative to that of lithium borohydride (238a).

In a manner analogous to some of the above addition reactions triphenylphosphinemethylene interacts with diborane to form an inner salt (XXII) containing a C—B—H linkage (239).



A reaction of tetramethyldiborane with sodium in ammonia at low temperatures produces the rather interesting salt (XXIII) according to Eq. (91) (166).



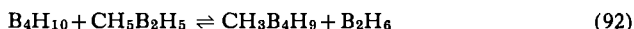
The salt $Na_2HB(CH_3)_2$ is stable as a white solid *in vacuo* up to $90^\circ C$, however, it hydrolyzes rapidly and quantitatively to $(CH_3)_2BOH$, $2H_2$, and $2NaOH$. Dissolved in liquid ammonia, it is yellow, diamagnetic, well-ionized, and unstable relative to disproportionation, a reaction that is promoted by tetramethyldiborane. In dimethyl ether, in which it is highly aggregated, (XXIII) is a ready source of hydride ion, easily converting chlorosilane to silane. In liquid ammonia the anion of the salt acts as a Lewis base, bonding with trimethylborane to form the compound $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$ which is stable up to $100^\circ C$ *in vacuo* (166). The calcium salt, $CaHB(CH_3)_2NH_3$, prepared in a manner analogous to the sodium salt, does not form an adduct with trimethylborane (240, 241).

B. Tetraborane Derivatives

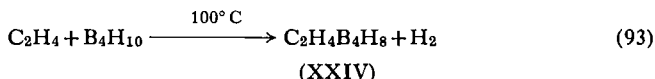
1. Alkyltetraboranes

A methyltetraborane has been obtained in low yield from an exchange reaction between tetraborane and a mixture of monomethyldiborane and dimethyldiboranes. Infrared evidence supports the assignment of the methyl

group to the 2-position (242). Attempts to prepare ethyltetraborane through an analogous exchange between ethyldiboranes and tetraborane



(243) or from ethylene and tetraborane have been unsuccessful. However, a reaction between the latter two compounds in a hot-cold reactor has been reported to give 2,4-dimethylenetetraborane (XXIV) in good yield (244).



The cyclic bridge structure (Fig. 2) proposed for this compound on the basis of infrared evidence has been confirmed by B^{11} and H^1 nuclear

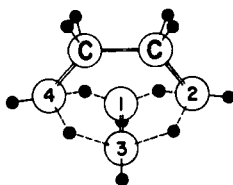
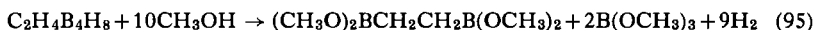
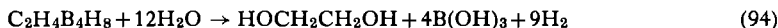


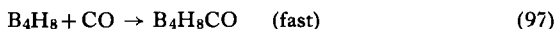
FIG. 2. Structure of 2,4-dimethylenetetraborane.

magnetic resonance studies (245). Consistent with this structural assignment, oxidative hydrolysis and methanolysis of 2,4-dimethylenetetraborane produces ethylene glycol and 1,2-bis(dimethoxybora)ethane, respectively (244).

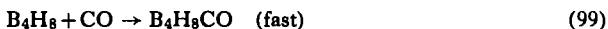
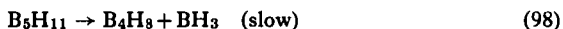


2. Carbon Monoxide-(C—B)Tetraborane(8)

The compound carbon monoxide-(C—B)tetraborane(8) (12), $\text{B}_4\text{H}_8\text{CO}$, is prepared by the action of carbon monoxide on either B_5H_{11} (102, 246) or B_4H_{10} (102, 247). The latter reaction is first order in tetraborane(10) and zero order with respect to carbon monoxide, suggesting a slow step [Eq. (96)] followed by a fast combination of the resulting B_4H_8 with carbon monoxide [Eq. (97)] (102, 247). Similarly, the reaction of carbon monoxide with

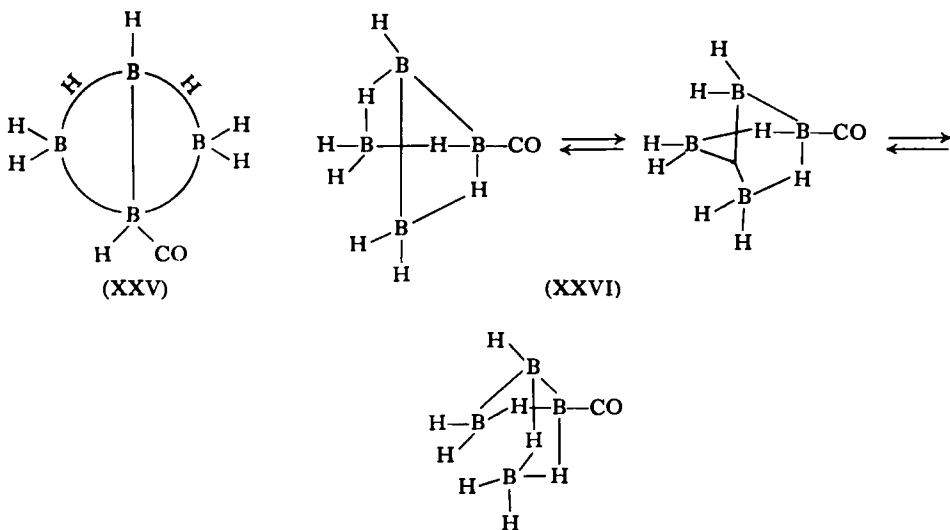


pentaborane(11) probably involves a slow cleavage [Eq. (98)] with subsequent formation of the appropriate carbonyl adducts of the intermediate boron hydride species.

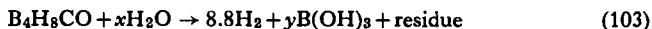


The reversibility of these reactions is evidenced by the high yields of B_4H_{10} and B_5H_{11} when H_2 or B_2H_6 reacts with $\text{B}_4\text{H}_8\text{CO}$ (102).

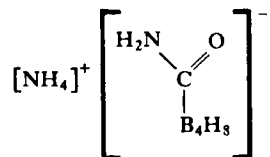
The infrared spectrum of $\text{B}_4\text{H}_8\text{CO}$ includes a carbon-oxygen stretching band very similar to that of BH_3CO (Section II,A,5) which suggests a parallel kind of B—C—O bonding. Two structures (XXV) and (XXVI) have been suggested as being consistent with the B^{11} nuclear magnetic resonance spectrum. A tautomerism similar to that in B_5H_{11} is considered in structure (XXVI).



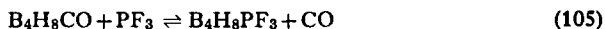
A number of basic reagents attack $\text{B}_4\text{H}_8\text{CO}$ to form nonvolatile materials without liberation of carbon monoxide (102, 237).



On the basis of largely chemical evidence, the structure of $B_4H_8CO \cdot 2NH_3$ appears to be analogous to that of $BH_3CO \cdot 2NH_3$ (237).



A reversible (102) displacement of carbon monoxide from B_4H_8CO is observed with PF_3 (248).



A similar displacement is observed with the use of $F_2PN(CH_3)_2$ (248a).

It is interesting that ethylene did not displace carbon monoxide from the tetraborane(8)-carbonyl with formation of $B_4H_8C_2H_4$ (244). Instead, the two reagents combined in a ratio of 4:1 to form $(C_2H_4)_4B_4H_8CO$ of undetermined structure (102).

C. Pentaborane(9) Derivatives

Alkylation of the apical boron atom in pentaborane(9) is effected by olefins or alkyl halides in the presence of a Lewis acid catalyst such as aluminum chloride (249–254). (Fig. 3). Alternatively, trialkylborates (255),

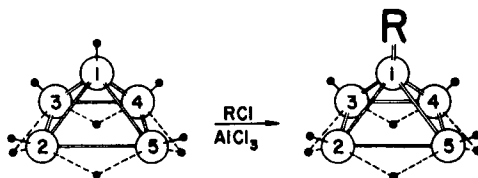
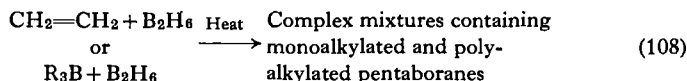
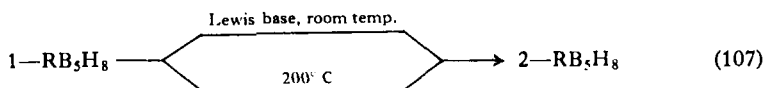
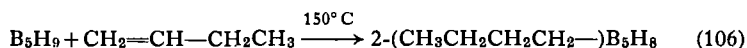


FIG. 3. The Friedel-Crafts synthesis of 1-alkylpentaborane(9).

alkyl ethers (256, 257), and alkyl silicates (258) have been utilized as alkylating agents. Multiple alkylation of pentaborane does not occur under the conditions of this modified Friedel-Crafts reaction (249) even when drastic conditions are imposed (259). This can be considered as supporting evidence that the acid-catalyzed alkylation reaction results in substitution at the chemically unique apical boron atom. However, the site of substitution is unambiguously established by B^{11} and H^1 nuclear resonance (251). The high-field doublet (apical B—H) in the B^{11} NMR of pentaborane collapses to a singlet and shifts to lower field (B—R) (251, 260); and the high-field quartet (apical H—B) in the H^1 NMR of pentaborane disappears entirely

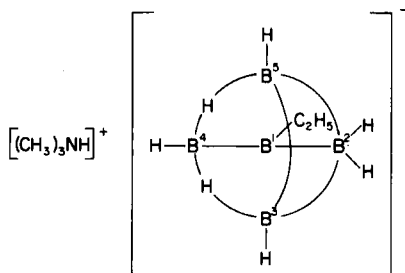
(251). Other known acid-catalyzed pentaborane substitution reactions also result in apically substituted pentaboranes (251, 261–263). This is in agreement with the predicted site of electrophilic substitution based on charge distributions, as determined from valence bond and molecular orbital treatments (17, 264, 265). Furthermore, the position of observed attachment of boron on the carbon skeleton (i.e., the most substituted carbon when unsymmetrical alkenes are used) is consistent with this predicated mechanism (249). The position of boron attachment is kinetically rather than thermodynamically controlled, for basal substituted alkylpentaboranes are found to be about 3 kcal/mole more stable than the corresponding apically substituted pentaboranes (266).

There are several different methods [Eqs. (106)–(108)] by which 2-alkylated pentaboranes can be prepared. The reaction of pentaborane at elevated



temperatures with olefins in the absence of a catalyst (267) gives good conversions but poor yields of the appropriate 2-alkylpentaboranes. The position of attachment of the boron atom on the carbon skeleton (least substituted when unsymmetrical olefins are used), as well as the basal substitution on the pentaborane pyramid, are in accord with a proposed mechanism of nucleophilic attack by the olefin (267). The small positive charge assigned to each basal boron atom in pentaborane from valence bond and molecular orbital treatments (17, 264, 265), in contrast to the negative charge assigned to the apical boron, gives theoretical support to this mechanism.

With the use of a sterically hindered Lewis base such as 2,6-dimethylpyridine a rearrangement of 1-alkylpentaboranes to the corresponding 2-alkylpentaboranes is effected at room temperature without noticeable build-up of an intermediate species (260). On the other hand, use of a relatively strong base such as trimethylamine converts the alkylpentaborane to an intermediate salt (XXVII) which yields the more stable 2-alkylpentaborane isomer on treatment with an appropriate acid (268). It is proposed



(XXVII)

(268) that the Lewis-base-catalyzed isomerization of alkylpentaboranes proceeds through such an intermediate ion, rather than *via* a symmetrical cleavage (260) or an intramolecular symmetrical semicleavage mechanism (17, 269). It is unlikely that the thermal rearrangement of 1-alkylpentaboranes proceeds by such an ionic intermediate, although the alkyl-boron migration is undoubtedly intramolecular (259). However, on the basis of isotopic exchange studies, an intermolecular hydrogen exchange presumably accompanies, or perhaps is responsible for, the thermal isomerization (270). A boron-boron exchange has been observed on treating the 1:2 adduct of 1-methylpentaborane and trimethylamine with B^{10} -enriched diborane. The more stable 2-methylpentaborane is liberated and exhibits B^{10} -enrichment in all positions except B(2) (270a).

Pyrolysis of ethylene-diborane and trimethylborane-diborane mixtures (271, 272) yields 2-alkylpentaboranes, as well as mixtures of polyalkylated pentaboranes and alkylated decaboranes. The B^{11} NMR data for the alkylated pentaboranes obtained from the ethylene-diborane reaction (271) should be reinterpreted in favor of a downfield chemical shift effect of the alkyl group.

The alkylpentaboranes are sensitive to air oxidation and to hydrolysis, the derivatives with smaller alkyl groups resembling pentaborane(9) more closely in this respect (249, 267). Known alkylpentaboranes are summarized in Table III.

The reaction of pentaborane(9) with alkynes to form carboranes is reviewed in Section III.

D. Pentaborane(11) Derivatives

Reversible exchange at ambient temperatures between pentaborane(11) and monoalkyldiboranes, or 1,2-dialkyldiboranes, provides a convenient

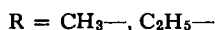
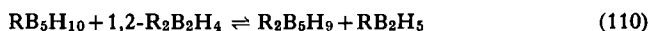
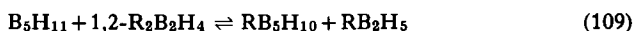
TABLE III
ALKYL DERIVATIVES OF PENTABORANE(9)

Compound	Physical properties			
	B.p. (°C/mm)	M.p. (°C)	Other	References
1-Methylpentaborane(9)	75.2° 0°/35	−56° to −55°	IR (251), B ¹¹ NMR (259)	249 272
1-Ethylpentaborane(9)	106° 104°	−85° to −84° −85°	IR, H ¹ NMR (251) B ¹¹ NMR (251, 260)	249 250
1-Isopropylpentaborane(9)	124°	−93.5° to −92.5°	—	249
1- <i>sec</i> -Butylpentaborane(9)	148°	—	—	249
1-Methyl-2- <i>sec</i> -butylpentaborane(9)	164°	—	—	249
2-Methylpentaborane(9)	0°/20.2	—	IR (272), B ¹¹ NMR (259)	272
2-Ethylpentaborane(9)	—	—	B ¹¹ NMR (260)	259, 260, 267
1,2-Dimethylpentaborane(9)	—	—	B ¹¹ NMR	259
2- <i>n</i> -Butylpentaborane(9)	154.5°	—	—	267
2- <i>sec</i> -Butylpentaborane(9)	150°	—	—	267
2-Isobutylpentaborane(9)	152°	—	—	267
Di-(1-pentaboryl)methane	88°/14	50.8°–51.8°	IR	263
(1-Pentaboryl)dichloroborylmethane (B ₅ H ₈)CH ₂ BCl ₂	—	—	IR	263

TABLE IV
 ALKYL DERIVATIVES OF PENTABORANE(11)

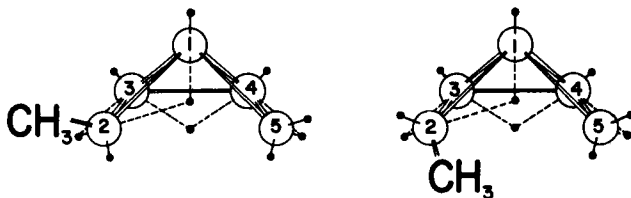
Compound	Physical properties		References
	B.p. (° C/mm)	Other	
2-Methylpentaborane(11) 2-CH ₃ B ₅ H ₁₀	0°/21	MS, IR, H ¹ NMR	242
Dimethylpentaborane(11) (CH ₃) ₂ B ₅ H ₉	—	MS, IR	242
2-Ethylpentaborane(11) C ₂ H ₅ B ₅ H ₁₀	0°/5	IR (274)	243, 274
Diethylpentaborane(11) (C ₂ H ₅) ₂ B ₅ H ₉	0°/0.5	—	243, 274

method for obtaining monoalkyl and dialkylpentaborane(11) derivatives (see Table IV) (242, 243).



The nature of this reaction appears consistent with the previously reported isotopic exchange between diborane and pentaborane(11) (273). Other methods include the direct interaction of ethylene with pentaborane(11) at 25° C (274), and a reaction at elevated temperatures (100° C) between tetraborane and a methyl diborane mixture (242). From H¹ NMR and infrared evidence (242, 274) the monoalkylated product is most probably 2-alkylpentaborane(11). The presence of two methyl resonances in the H¹ NMR of 2-methylpentaborane(11) is attributed to a mixture of the possible *exo* and *endo* forms (Fig. 4) (242).

Although the structure of the dialkyl derivative of pentaborane(11) has not been unambiguously determined, it is believed that the two alkyl groups are attached to different boron atoms. This assignment is partially supported

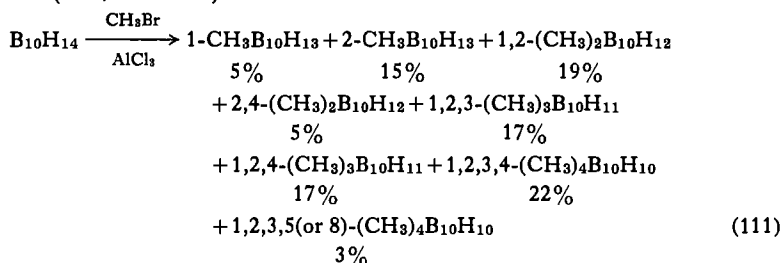

 FIG. 4. *Exo* and *endo* forms of 2-alkylpentaborane(11).

by the inability of B_5H_{11} to exchange with 1,1-diethyldiborane. However, this unobserved exchange may involve an unfavorable rate rather than an unfavorable equilibrium (243).

Products which can be predicted on the basis of the above equilibria [Eqs. (109) and (110)] and from known pentaborane(11) chemistry have been isolated from decomposition studies on the alkylated pentaboranes(11). One such decomposition gave evidence for formation of a trialkylated pentaborane(11) (242).

E. Decaborane(14) Derivatives

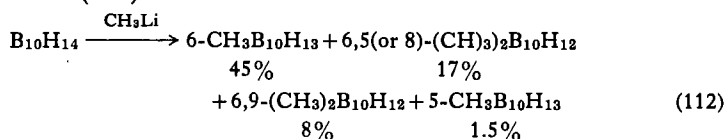
In contrast to the monoalkylation of pentaborane(9), Friedel-Crafts alkylation of decaborane(14) with alkyl halides or olefins yields a mixture of derivatives (250, 275-282).



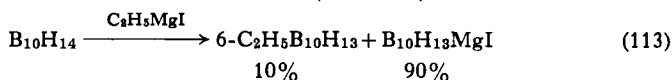
However, the preferred boron sites of this presumed electrophilic substitution are in accordance with the regions of high charge density, as computed by molecular orbital calculations (17).

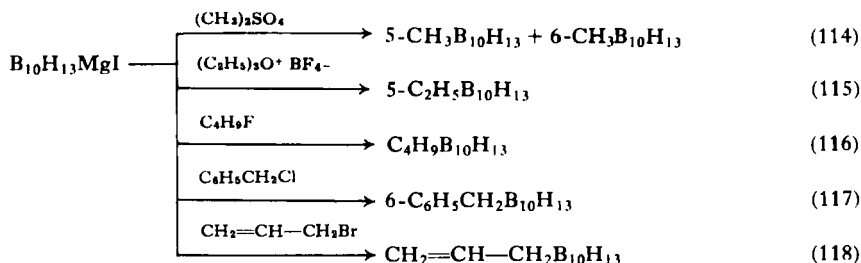
Position	2,4	1,3	5,7,8,10	6,9
Charge	-0.10	-0.04	+0.12	+0.33

Conversely, the 6,9 and 5,7,8,10-positions are the preferred sites of nucleophilic substitution (283).



Grignard reagents also give the expected 6-alkylated decaboranes, but in low yield (284). The major product, instead, is a rather novel Grignard reagent, decaboranylmagnesium iodide, which in turn reacts with a variety of compounds to form decaborane derivatives (284-287).





In a similar fashion the $\text{B}_{10}\text{H}_{13}^-$ ion, prepared from sodium hydride and decaborane, reacts with methyl and ethyl sulfate (288) and benzyl chloride (288, 289) to give the same substituted decaboranes as are obtained from the decaboranyl Grignard reagent.

Pyrolysis of an ethylene-diborane mixture has yielded a complex product which contains, in addition to alkylated pentaboranes (Section II, C), a mixture of mono- (probably 5-substituted), di-, tri, and tetraethyldecaboranes (271).

Although no B^{11} NMR chemical shift data are available for the various alkylated decaboranes, a comparison of published spectra with that of decaborane usually reveals the position of attachment in a rather direct fashion (250, 271, 275, 283-285, 289). Unfortunately, the resonance lines of the 1,3 and 6,9-positions overlap. However, it has generally been observed that 6-alkyldecaboranes (Fig. 5) can be differentiated from 1-alkyldeca-

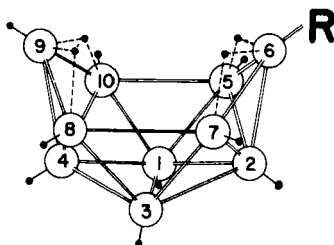


FIG. 5. Ball and stick model of 6-alkyldecaborane.

boranes simply by observing changes in the resonance lines of the apical 2- and 4-positions of $\text{B}-\text{H}$. The high field doublet ($\text{B}-\text{H}$ coupling) assigned to the chemically equivalent 2,4-positions in decaborane remains as a single doublet structure in the 1-substituted compound, whereas

in the 6-substituted compound the 2- and the 4-positions, no longer equivalent, are observed as two sets of closely spaced doublets (283–285).

The alkyldecaboranes, like decaborane, can be titrated as monoprotic acids in acetonitrile (275, 283). In the presence of cineole, the four bridge hydrogens of 6-benzyldecaborane exchange rapidly with deuterium oxide. This is followed by an exchange of three other hydrogens (probably 8-, 9-, and 10-positions), and eventually the remaining six terminal hydrogens (289).

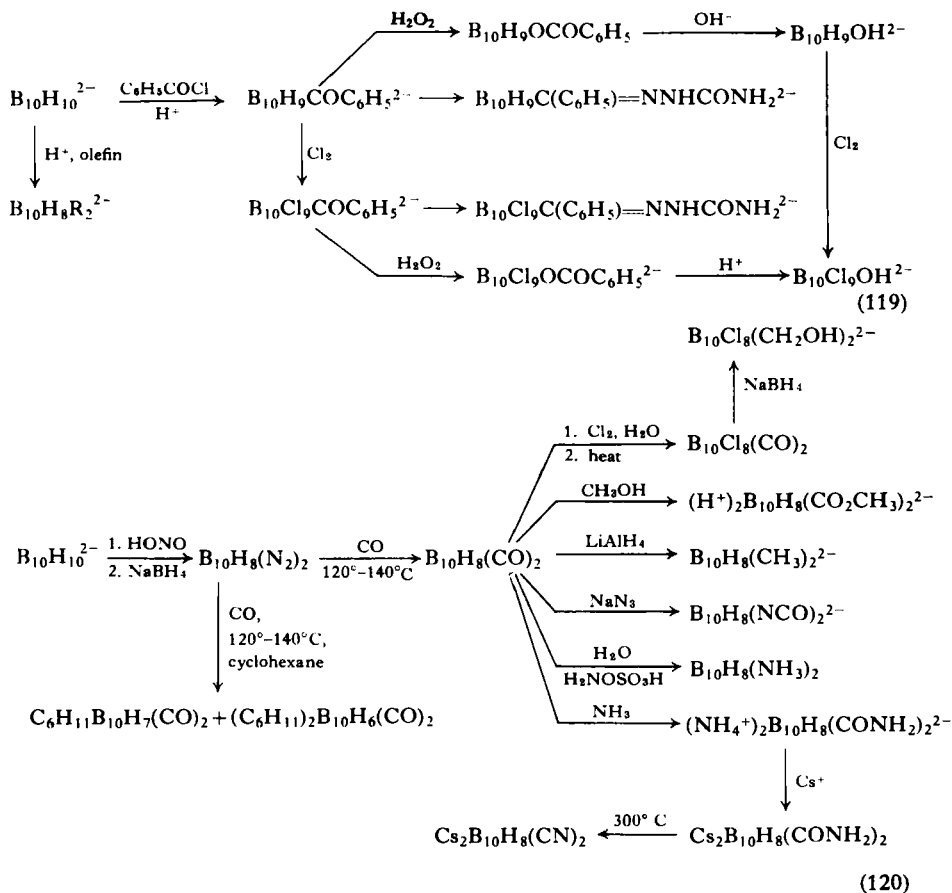
Mono-, di-, tri-, and tetraethyldecaboranes react with alkyl cyanides and other ligand molecules (292) to give materials (293) which are most likely related to bis(acetonitrile)decaborane (294, 295). In contrast to the B—N bonding in the latter compound, there is a possibility that carbon–boron bonds are formed from the reaction of cyanide ion with decaborane (238, 296).

TABLE V
DERIVATIVES OF DECABORANE

Compound	Physical properties		
	M.p. (°C)	Other	References
2-Methyldecaborane	4°–6°	B ¹¹ NMR	275
5-Methyldecaborane	—	B ¹¹ NMR	284, 288
6-Methyldecaborane	27°–28°	B ¹¹ NMR	283, 284, 288
1-Ethyldecaborane	1°–2°	X-ray	290
5-Ethyldecaborane	1°–2°	B ¹¹ NMR (271, 284), IR (271)	271, 284, 288
6-Ethyldecaborane	–2.5° to –2°	—	283, 284, 288
6-Benzyldecaborane	63.5°–64.5°	IR (285) MS (289) B ¹¹ NMR (285)	284, 285, 288, 289, 291
Cyclohexyldecaborane	90°–91°	—	286
Allyldecaborane	—	η_D^{25} 1.5652	287
1,2-Dimethyldecaborane	–40° (glass)	B ¹¹ NMR	275
2,4-Dimethyldecaborane	43.5°–44.5°	B ¹¹ NMR	275
6,5(or 8)-Dimethyldecaborane	26.5°–28.5°	B ¹¹ NMR	283
6,9-Dimethyldecaborane	64°–65°	B ¹¹ NMR	283
1,2-Diethyldecaborane	—	B ¹¹ NMR	250
2,4-Diethyldecaborane	—	B ¹¹ NMR	250
Dibenzyldecaborane	111°–116°	MS	289
1,2,3-Trimethyldecaborane	161°–163°	B ¹¹ NMR	275
1,2,4-Trimethyldecaborane	12°–13°	B ¹¹ NMR	275
1,2,3,4-Tetramethyldecaborane	178°–179°	B ¹¹ NMR	275
1,2,3,5(or 8)-Tetramethyldecaborane	70°–71°	B ¹¹ NMR	275

Derivatives of decaborane are listed in Table V. Carborane formation from decaborane and acetylenes is summarized in Section III.

An abundance of organic derivatives of the polyhedral (301) $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions (302, 303) has recently been reported (304-306). This



can be partially attributed to the development of one-step syntheses of the parent ions from monoboron compounds (307, 308). Many of the reactions encountered for these ions are very reminiscent of aromatic hydrocarbon chemistry, as is illustrated in the following equations (304–306, 308a–308c). A similarity will also be noticed between the products of the Lewis base reactions of $B_{10}H_8(CO)_2$ and those of BH_3CO (Section II,A,5) and of B_4H_8CO (Section II,B,2).

Whereas the inner diazonium salt $B_{10}H_8(N_2)_2$ and the dicarbonyl $B_{10}H_8(CO)_2$ are 1,10-substituted, the benzoyl derivative (Fig. 6) is predominantly the equatorial isomer.

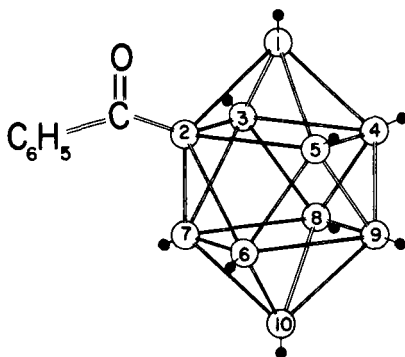
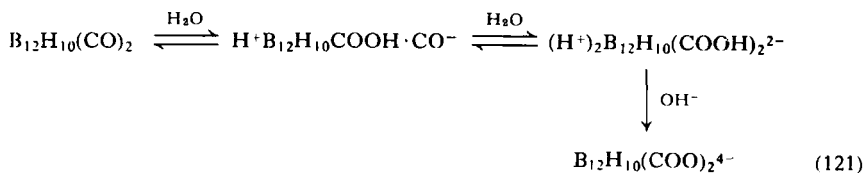


FIG. 6. Structure of the 6-benzoyl derivative of $B_{10}H_{10}^{2-}$.

In water the intermediate carbonyls are in equilibrium with carboxylic acid derivatives, which are isolated as salts. Acidity function studies indicate carboxyl proton ionization constants of about 10^{-9} (305).



III

CARBORANES

As mentioned previously (Section I), the term "carborane" is used to designate a C—B—H system in which *the carbon atoms are an integral part* of the skeletal framework. At present, only carboranes with two carbon

skeletal atoms are known; however, it is to be anticipated that systems with a differing number of carbon atoms but within the general formula $C_nB_mH_{n+m}$ will be prepared in the future. Additional characteristic features of the carboranes include the polyhedral arrangement of atoms and the absence of bridge hydrogens so commonly present in the boron hydrides. The dihydrocarboranes (Section III,B), with two extra hydrogens present in bridge positions, may be loosely considered a hydrid of the carborane and boron hydride structural patterns.

An extensive review of bonding principles used to describe the carboranes and related systems is now available (17). For the purpose of the present discussion a simplified molecular orbital approach (17, 309–311) is briefly outlined. In this treatment it is convenient to initially examine the $B_nH_n^{2-}$ ions which are considered to be isoelectronic with the two-carbon carboranes. The hypothetical $B_5H_5^{2-}$, $B_6H_6^{2-}$, and $B_7H_7^{2-}$ ions can be pictured with an equatorial belt of planar B—H units joined by σ bonds, and a π -electron set of molecular orbitals which combine with the appropriate combination of orbitals formed from the additional B—H units above and below the equatorial plane (Fig. 7).² By removing the apical B—H groups from the poly-

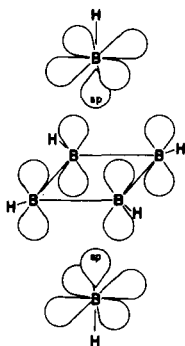


FIG. 7. Simplified description of bonding in $B_6H_6^{2-}$ (isoelectronic with $C_2B_4H_6$).

hedral $B_5H_5^{2-}$ (isoelectronic with $C_2B_3H_5$), $B_6H_6^{2-}$ ($C_2B_4H_6$), and $B_7H_7^{2-}$ ($C_2B_5H_7$) ions the remaining planar $B_3H_3^{2-}$, $B_4H_4^{2-}$, and $B_5H_5^{2-}$ units can be treated by the usual molecular orbital methods employed for aromatic hydrocarbons.

A similar approach has been used for the pyramidal $B_nH_n^{4-}$ ions. Such highly charged species are not expected to be particularly stable. However

² The ion $B_6H_6^{2-}$ has recently been isolated and characterized (311a).

this drawback can be remedied by replacing C for B⁻ and/or by adding H⁺ to the edge-single B—B bonds to produce bridge H atoms. Such modifications predict pyramidal C₄B₂H₆ and C₄BH₅ molecules as well as the known C₂B₄H₈ (Section III, B, 1).

TABLE VI
GEOMETRIES OF C_nB_{6-n}H₆ MOLECULES AND IONS^a

	<i>n</i> = 6	<i>n</i> = 4	<i>n</i> = 2	<i>n</i> = 0
Planar	C₆H₆	C ₄ B ₂ H ₆ ²⁻	—	—
Pyramidal	—	C ₄ B ₂ H ₆	C ₂ B ₄ H ₆ ²⁻	B ₆ H ₆ ⁴⁻
Bipyramidal	—	C ₄ B ₂ H ₆ ²⁺	C₂B₄H₆	B₆H₆²⁻

^a Bold face formulas represent known systems; the others have been considered or implied by Lipscomb (17).

In Table VI known and predicted molecules and ions having the general formula C_nB_{6-n}H₆ are classified in terms of their known or expected geometries. Logical extensions of the above correlations suggest bipyramidal CB₅H₆⁻, pyramidal C₃B₃H₆⁻, and planar C₅BH₆⁻ ions, among others.

Thus, far, all of the known carboranes have been derived either directly or indirectly from reactions of alkynes with various boron hydrides. In these reactions only the carbons participating in the triple bond of the alkyne become skeletal atoms in the carborane. No routes to the hypothetical four-carbon carboranes have been suggested. However, the dehydrogenation of the cyclic diborane derivatives prepared from butadiene (98, 100) should lead to C₄BH₅ and C₄B₂H₆. Unfortunately, such a conversion may require electric discharge conditions, in which case extremely low yields can be expected.

A. "Small" Carboranes: C₂B₃H₅, 1,2-C₂B₄H₆, 1,6-C₂B₄H₆, and C₂B₅H₇

1. 1,5-Dicarbaclovopentaborane(5), C₂B₃H₅

Reactions between acetylene and either diborane (312) or pentaborane(9) (313, 314) in a silent electric discharge afford small but sufficient quantities of the carborane C₂B₃H₅ for nuclear magnetic resonance and infrared analyses. Recently, improved yields of the compound have been obtained from the electric discharge of 2,3-dicarbaclovohexaborane(8) (315). From

available spectroscopic data $C_2B_3H_5$, the smallest of the known carboranes, is assigned a trigonal bipyramidal structure (Fig. 8) with a carbon atom at

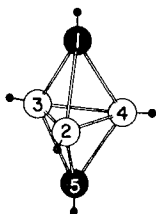


FIG. 8. Ball and stick model of 1,5-dicarboclovopentaborane(5).

each of the two apices (313, 314). This geometry is consistent with the presumed structure of the hypothetical isoelectronic $B_5H_5^{2-}$ ion (310).

Interestingly, of the three possible $C_2B_3H_5$ isomers having a trigonal bipyramidal framework, the one isolated, 1,5-dicarboclovopentaborane(5), was predicted to be the most stable, based on molecular orbital and resonance considerations (17, 316).

1,5-Dicarboclovopentaborane(5) is stable up to about 150°C , at which temperature it slowly decomposes affording tan solids and hydrogen (315). When allowed to come into contact with acetone, trimethylamine, carbon dioxide, air, or water at room temperature no noticeable reaction ensues, which is in contrast to the reactivity of most boron hydrides with these reagents. The deuterium in deuteriodiborane exchanges with the three hydrogens bonded to the boron atoms, but not with the hydrogens bonded to the carbon atoms (314).

Recently, *B,B,B*-triethyl-*C,C*-dimethyl-1,5-dicarboclovopentaborane(5) has been isolated from a reaction of tetraethyldiborane with acetylene (316a).

2. 1,6- and 1,2-Dicarboclovohexaboranes(6), $C_2B_4H_6$

Two compounds having the composition $C_2B_4H_6$ have been isolated from the electric discharge of acetylene-diborane or acetylene-pentaborane mixtures (313, 314, 317), as well as from the electric discharge of 2,3-dicarboclovohexaborane(8) (315) (Section III,B,1). The B^{11} and H^1 nuclear magnetic resonance, infrared, and mass spectra are consistent with the suggested octahedral (tetragonal bipyramid) structures for both molecules. In this case both isomeric possibilities (Fig. 9) are realized: the *trans* or sym-

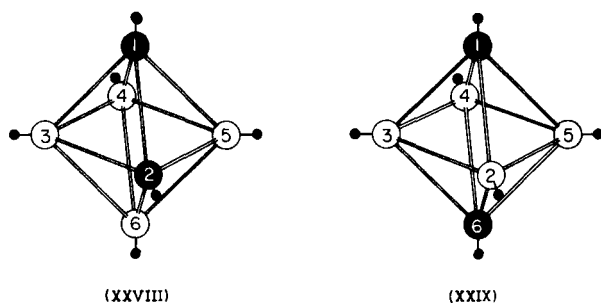


FIG. 9. Ball and stick models of the two isomers of $C_2B_4H_6$.

metrical isomer, 1,6-dicarbaclovohexaborane(6) (XXVIII), and the *cis* or unsymmetrical isomer, 1,2-dicarbaclovohexaborane(6) (XXIX) (313, 317).

In both compounds each carbon atom appears to be bonded to five instead of the customary four atoms. To circumvent this anomaly the concept of carbon participating in delocalized two- and three-center bonds is invoked (17, 316). From the H^1 NMR a shielding constant of about 1.1 has been determined for the 1,6-dicarbaclovohexaboranyl(6) group bonded at a skeletal carbon atom (315).

Contrary to a previous impression (317), 1,2-dicarbaclovohexaborane(6) can be quantitatively rearranged at about $250^\circ C$ to the more symmetrical isomer, 1,6-dicarbaclovohexaborane(6) (315), as predicted (313, 318). The 1,6-isomer can remain in contact with acetone, trimethylamine, ammonia, air, and water at room temperature without noticeable reaction. The hydrogen atoms attached to the boron atoms will undergo H-D exchange with deuteriodiborane at room temperature, but the exchange rate is less rapid than a similar exchange with 1,5-dicarbaclovopentaborane(5) (previous section) (317).

C-Alkylated derivatives of 1,6-dicarbaclovohexaborane(6) (XXVIII) are obtained in modest yield from the pyrolysis of corresponding C-alkylated 2,3-dicarbaheptaborane(8) derivatives (Section III, B, 1) in the presence of trimethylamine. Since temperatures above $250^\circ C$ are required for the conversion, it is not surprising that C-alkylated derivatives of 1,2-dicarbaclovohexaborane(6) (XXIX) are absent from the product mixture. The absence of trimethylamine during the pyrolysis significantly decreases the yield of C-alkylated 1,6-dicarbaclovohexaborane(6) and favors, instead, another major volatile product, C-alkylated 2,4-dicarbaclovoheptaborane(7) (Section III, A, 3). Apparently, the unshared electrons of trimethylamine

play an important part in determining the course of the pyrolysis, for it is established that the effect of this amine as a diluent is negligible (319).

3. 2,4-Dicarbaclovoheptaborane(7), $C_2B_5H_7$

In addition to the small carboranes mentioned above (Sections III,A,1 and 2), the silent electric discharge of diborane–acetylene or pentaborane–acetylene mixtures produces a compound of composition $C_2B_5H_7$, in low yield. The B^{11} and H^1 nuclear magnetic resonance and infrared spectra (313, 319) of this compound indicate that there are no bridge hydrogens and that there are three different boron environments in the ratio 2:2:1. Within the proposed (313) pentagonal bipyramidal arrangement this eliminates a symmetrical structure with carbon at the apices of a five-boron mutual base. Of the three possible structural isomers remaining, chemical arguments favor a structure (Fig. 10) in which the two carbon atoms are non-

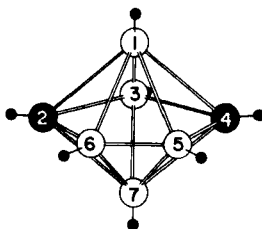


FIG. 10. Ball and stick model of 2,4-dicarbaclovoheptaborane(7).

adjacent (319). Recently, microwave studies have confirmed this structural assignment and, in addition, provided bond distances: $B(1)-C(2) = 1.708 \pm 0.05$ Å; $B(1)-B(3) = 1.818 \pm 0.05$ Å; $B(1)-B(5) = 1.815 \pm 0.05$ Å; $C(2)-B(3) = 1.546 \pm 0.05$ Å; $C(2)-B(6) = 1.563 \pm 0.05$ Å; $B(5)-B(6) = 1.651 \pm 0.05$ Å; $B-H = 1.20$ Å; $C-H = 1.09 \pm 0.05$ Å (320).³

From H^1 NMR studies an approximate shielding constant of 1.8 has been determined for the 2,4-dicarbaclovoheptaboranyl(7) group bonded at a carbon atom (315).

Thermal decomposition of the appropriate 2,3-dicarbahexaborane(8) (Section III,B,1) at about $300^\circ C$ is, at present, the best laboratory method for preparing 2,4-dicarbaclovoheptaborane(7) and its *C*-alkyl derivatives (315, 319). Neither this pyrolysis reaction, nor the previously mentioned

³ The bond distances cited are based upon recent microwave studies by the same authors on the C^{13} -labeled material (to be published).

TABLE VII
THE "SMALL" CARBORANES AND DIHYDROCARBORANES

Compound	Reference	M.p. (°C)	B.p. (0°C/mm)	B ¹¹ NMR		H ¹ NMR		
				δ^a	\mathcal{J} (cps)	δ^b	\mathcal{J} (cps)	
1,5-Dicarblovopentaborane(5) C ₂ B ₃ H ₅	313, 314	-126.4	-3.7	B—H C—H	-1.4 —	183-184 (314, 315, 317)	-2.9 -4.65	188 (314, 315)
1,2-Dicarblovohexaborane(6) unsym-C ₂ B ₄ H ₆	313, 317	—	—	B(3,5) or B(4,6)—H B(4,6) or B(3,5)—H C—H	+1.6 +15.3 —	174-178 (315, 317) 187-195 —	-1.82 — -2.87	178 (315, 317)
1,6-Dicarblovohexaborane(6) sym-C ₂ B ₄ H ₆	313, 317	-32.6	22.7	B—H C—H	+19.4 —	188-189 (317, 319)	-1.92 -3.14	187 (315, 317)
C,C'-Dimethyl-1,6-dicarblovohexaborane(6)	319	-2° to -1	—	B—H C—CH ₃	+16.3 —	185	-1.83 -1.33	184
C- <i>n</i> -Propyl-1,6-dicarblovohexaborane(6)	319	-88° to -87°	—	B—H C—H C—CH ₂ CH ₂ CH ₃	+18.6 — —	186 — —	-193 -2.87 -1.77	187 — -1.42 and -0.94
2,4-Dicarblovohexaborane(7)	313, 315	—	—	B(3)—H B(5,6) or B(1,7)—H B(1,7) or B(4,5)—H C—H	-5.0 -2.0 +23.5 —	187 (319) 170 178 —	-4.75 -4.00 -0.15 -5.50	183 (315) 171 177 —
C,C'-Dimethyl-2,4-dicarblovohexaborane(7)	319	-30° to -28°	—	B(3)—H B(5,6) or B(1,7)—H B(1,7) or B(4,5)—H C—CH ₃	-5.6 -4.5 +19.5 —	177 165 176 —	-4.46 -3.67 -0.18 -2.02	176 165 175 —
C- <i>n</i> -Propyl-2,4-dicarblovohexaborane(7)	319	-99° to -97°	—	B(3)—H B(5,6) or B(1,7)—H B(1,7) or B(4,5)—H C—H C—CH ₂ CH ₂ CH ₃	-5.2 -4.0 +21.0 — —	176 170 176 — —	-5.2 -4.1 -0.2 -5.35 -2.43	180 ? 179 — -1.57 and -0.87
2,3-Dicarbhaexaborane(8) C ₂ B ₄ H ₈	321	—	—	B(1)—H B(4,5,6)—H C—H B—H _{bridge} —B	+54.0 ~ +3.0 — <i>c</i>	179 (315) 158 — <i>c</i>	+1.13 -3.44 -6.32 +2.6	181 (315) 158 — —
C-Methyl-2,3-dicarbhaexaborane(8)	50, 315	—	—	B(1)—H B(4,5,6)—H ^c C—H C—CH ₃ B—H _{bridge} —B	+49.9 ~ +3.6 — — <i>c</i>	175 (50) ~ 152 — — <i>c</i>	+0.81 -3.45 -6.16 -2.27 -2.3	179 (315) 158 — — —

C,C'-Dimethyl-2,3-dicarbahexaborane(8)	50, 319	-64° to -63°	25°/29.0 (322)	B(1)—H	+47.7	186 (50)	+0.92	178 (319)
				B(4,5,6)—H ^c	~ +5.4	~ 154	-3.20	156
				C—CH ₃	—	—	-2.07	—
				B—H _{bridge} —B	<i>c</i>	<i>c</i>	+2.4	—
C- <i>n</i> -Propyl-2,3-dicarbahexaborane(8)	50, 319	—	—	B(1)—H	+49.7	175 (50)	+0.85	180 (319)
				B(4,5,6)—H ^c	~ 3.3	156	-3.37	157
				C—H	—	—	-6.10	—
				C—CH ₂ CH ₂ CH ₃	—	—	-2.43	-157 and -0.87
				B—H _{bridge} —B	<i>c</i>	<i>c</i>	+2.4	—
C-Phenyl-2,3-dicarbahexaborane(8)	315	—	—	B(1)—H	+49.3	175	+1.08	182
				B(4,5,6)—H ^c	+5.1	~ 150	-3.05	168
				C—H	—	—	-5.75	—
				C—C ₆ H ₅	—	—	-6.53	—
				B—H _{bridge} —B	<i>c</i>	<i>c</i>	+2.6	—
C-Isopropenyl-2,3-dicarbahexaborane(8)	315	—	—	B(1)—H	+50.6	175	+0.76	180
				B(4,5,6)—H ^c	+3.9	~ 155	-3.53	158
				C—H	—	—	-6.27	—
				C—C(CH ₃)=CH ₂	—	—	-1.93	-5.06 and -5.38
				B—H _{bridge} —B	<i>c</i>	<i>c</i>	+2.2	—

^a δ , ppm relative to boron trifluoride etherate (188).

^b δ , ppm relative to tetramethylsilane; negative values are to low field.

^c The B(4,6)—H doublet and B(5)—H doublet are nearly superimposable. In a reinterpretation of the 2,3-dicarbahexaborane(8) B¹¹ NMR (323) the low-field region consists of a broad doublet B(5)—H which is superimposed on a larger doublet B(4,6)—H with resolved splitting due to coupling to a single bridge hydrogen. The H_{bridge}—B(4,6) coupling constant is 44 cps in 2,3-dicarbahexaborane(8) but not well enough defined in C-phenyl-2,3-dicarbahexaborane(8) and C-isopropenyl-2,3-dicarbahexaborane(8) to be measured.

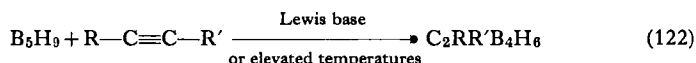
electric discharge reactions, lead to detectable amounts of the other possible $C_2B_5H_7$ isomers (e.g., 1,7-; 1,2-; 2,3-). It is interesting to note that the favored isomer (2,4-) in these reactions is the one predicted to be the most stable on the basis of molecular orbital and resonance considerations (17, 316).

The small carboranes (Sections III,A,1-3) and dihydrocarboranes (next section) are summarized in Table VII.

B. Dihydrocarboranes: $C_2B_4H_8$ and $C_2B_9H_{13}$

1. 2,3-Dicarbahehexaborane(8), $C_2B_4H_8$

Pentaborane(9) reacts with alkynes either at elevated temperatures (about 160°–210°C) or in the presence of a Lewis base catalyst to give 2,3-dicarbahehexaborane(8) derivatives (50, 315, 319, 321).



Increasing the number of alkyl groups about the alkyne triple bond enhances the reactivity toward pentaborane, and results in increased yields of the corresponding 2,3-dicarbahehexaborane(8) (315).

From B^{11} and H^1 NMR (50, 315, 323) and X-ray diffraction studies (51, 323a) $C_2B_4H_8$ is assigned a pentagonal bipyramidal structure (Fig. 11)

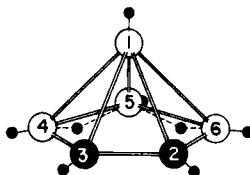


FIG. 11. Ball and stick model of 2,3-dicarbahehexaborane(8). Bond distances in the C,C' -dimethyl derivative: $B(1)-C(2) = 1.762 \text{ \AA}$; $B(1)-B(4) = 1.768 \text{ \AA}$; $B(1)-B(5) = 1.705 \text{ \AA}$; $C(2)-C(3) = 1.432 \text{ \AA}$; $C(2)-B(6) = 1.520 \text{ \AA}$; $B(4)-B(5) = 1.778 \text{ \AA}$ (51).

analogous to B_6H_{10} . In good agreement with the nearly trigonal hybridization assigned to the carbon atoms (51), the H^1 NMR spectrum of C^{13} -labeled $C_2B_4H_8$ gives a measured J_{C-H} of 160 cps (315). An "effective shielding constant" of about 1.8 has been determined for the 2,3-dicarbahehexaboranyl(8) group bonded at a skeletal carbon atom (315).

Pyrolysis of C -alkylated 2,3-dicarbahehexaborane(8) derivatives at about 290°–300°C gives principally C -alkylated 2,4-dicarbaheheptaborane(7)

derivatives (25–30%), and small amounts (2–5%) of the *C*-alkylated 1,6-dicarboclovohexaborane(6) compounds (319). The yield of the latter carborane is improved (20–25%) at the expense of the B₅ carborane when pyrolysis is carried out in the presence of trimethylamine. The absence of the 1,5-dicarboclovopentaborane(5) and 1,2-dicarboclovohexaborane(6) derivatives in these experiments is not surprising, for it has since been established that the former carborane decomposes at about 150°C and the latter rearranges at 250°C to the more stable *trans*(1,6-) isomer (315).

On subjecting C₂B₄H₈ to a silent electric discharge all the known small carboranes, C₂B₃H₅, 1,2-, and 1,6-C₂B₄H₆, and C₂B₅H₇, are formed in yields of about 3–5% (315). Although this is far from quantitative, it represents a marked improvement in the synthesis of C₂B₃H₅ and 1,2-C₂B₄H₆ over the direct electric discharge of pentaborane–acetylene mixtures (0.1–0.3% yields) (314, 317).

2. Dicarbaundecaborane(13), C₂B₉H₁₃

Dicarbaundecaborane(13) and its *C*-methyl and *C*-phenyl derivatives have been obtained by protonation of the corresponding dicarbaundecaborane salts (Section III, C, 10).



This new dihydrocarborane can be titrated as a monoprotic acid with an apparent pK_a of 2.95 in 33% (volume) methanol–water. It is suggested that the two skeletal carbons are adjacent in the pentagonal face of an icosahedral fragment (324).

Hydrogen is evolved from C₂B₉H₁₃ at temperatures above 100°C to give rise to a new carborane C₂B₉H₁₁ (324a, b).

C. Carborane: C₂B₁₀H₁₂

1. Preparation of 1,2-Dicarboclovododecaborane(12) from Alkynes and Decaborane

The interaction of acetylene with decaborane in the presence of a Lewis base affords 1,2-dicarboclovododecaborane(12) [Eq. (124)] which, unlike



conventional boron hydrides, is comparatively stable toward hydrolysis, air oxidation, and heating to at least 400°C (325–329). Alternatively, carborane may be prepared via a bis(ligand) derivative of decaborane [Eq. (125)], which

is, in all probability, an intermediate in Eq. (124). The generality of the reaction has been demonstrated by varying either the Lewis base or the



acetylenic component (325, 326, 330). Lewis bases such as acetonitrile, dialkyl sulfides, *N,N*-dimethylacetamide, *N,N*-dimethylaniline, tributylphosphine, and tetrahydrofuran have been used; however, when triethylamine is employed, a low yield of carborane is realized. It has been suggested (326) that under the conditions of the experiment the $[(\text{C}_2\text{H}_5)_3\text{N}]_2\text{B}_{10}\text{H}_{12}$ intermediate is converted to the ionic isomer $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{10}\text{H}_{10}$ which, presumably, would not lead to carborane. In the absence of a Lewis base no reaction occurs between decaborane and acetylenic compounds (326). Crude products, the C, B, H analyses of which are reminiscent of carboranes, have, however, been found upon subjecting acetylene and decaborane to about 250° C and 600 psig in the presence of a cuprous chloride catalyst (331).

C-substituted and C,C'-disubstituted carborane derivatives are prepared from the corresponding substituted acetylenes, $\text{RC}\equiv\text{CR}'$, where R and R' are variously H, alkyl, aryl, haloalkyl, carboalkoxy, or acetoxyalkyl. Lowest yields are encountered when both R and R' are alkyl groups (e.g., 2-butyne, 2-pentyne, 3-hexyne). Acetylenic alcohols and acids decompose the borane precursor rather than produce the substituted carborane. Esterification of these reactive groups, however, followed by the carboranylation reaction leads to satisfactory yields of the esterified carborane derivative (325, 326, 330). Although 1,6-heptadiyne can be converted to the biscarboranyl propane, certain diacetylenes such as the dibenzoate and the diacetate esters of 2,4-hexadiyne-1,6-diol afford the monocarborane as the major product, despite the use of excess borane (330). Both C-ethynylcarborane and bis(carborane) have been identified as products from a reaction between diacetylene and $\text{B}_{10}\text{H}_{12}(\text{CH}_3\text{CN})_2$ (332).

2. Structure and Stability

It has been proposed (17, 316, 318, 326, 333–336) that the $\text{C}_2\text{B}_{10}\text{H}_{12}$, obtained directly from the Lewis-base-catalyzed reaction between alkynes and decaborane, has very nearly the icosahedral geometry of the $\text{B}_{12}\text{H}_{12}^{2-}$ ion (301). The tendency of this carborane to form small C,C'-exocyclic rings (327, 334, 337–340) supports the contention that the two carbons are adjacent within the icosahedral framework (Fig. 12, XXX). An X-ray diffraction study (341) of the octachloro derivative, $\text{C}_2\text{H}_2\text{B}_{10}\text{H}_2\text{Cl}_8$ (342),

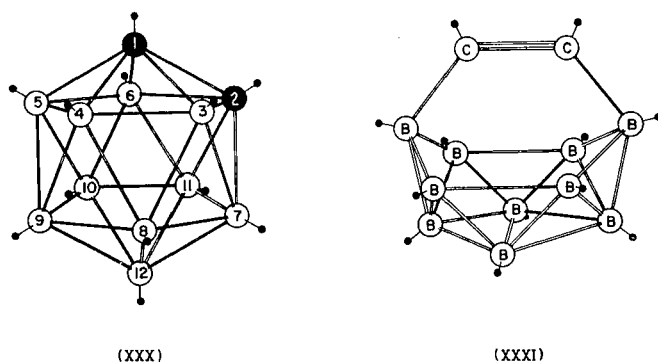


FIG. 12. Ball and stick models of 1,2- $C_2B_{10}H_{12}$. Structure (XXXI) is probably in error.

is in agreement with this structural assignment. The C—C distance of 1.68 Å in $C_2H_2B_{10}H_2Cl_8$ is significantly larger than the distance of 1.43 Å (51) in the C,C' -dimethyl derivative of $C_2B_4H_8$ (Section III,B,1) in which the carbon atoms are in a less strongly electron-deficient environment. In another X-ray diffraction study (343), a skeletal C—C distance of 1.40 Å has been reported for 1,2-bis(bromomethyl)carborane. Furthermore, this study suggests an ethylene decaborane type of C_2B_{10} unit (XXXI). On the basis of chemical (335, 339, 343, 344) and physical (336, 341, 342, 344, 344a) evidence, as well as on theoretical grounds (316, 318, 341), this latter work is probably in error.

The suggested icosahedral (or near icosahedral) arrangement of atoms for $C_2B_{10}H_{12}$ provides for three isomeric possibilities. Within the framework the two carbon atoms can be either adjacent (1,2-; *ortho*) (XXX) (325, 326, 342), intermediate (1,7-; *meta*) (XXXII, Fig. 13) (335, 336), or opposite

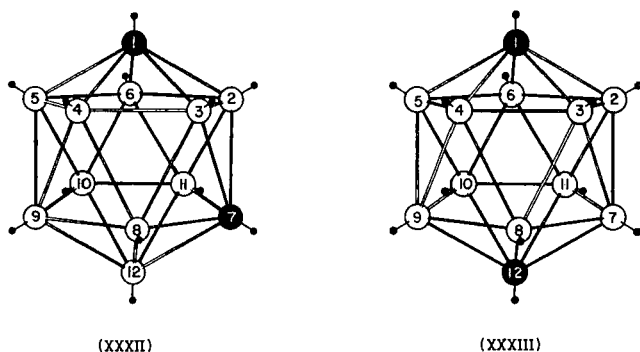


FIG. 13. Ball and stick models of 1,7- and 1,12- $C_2B_{10}H_{12}$.

(1,12-; *para*) (XXXIII) (345) to each other. Historically, *meta*-carborane has been called neocarborane and the unmodified term, carborane, has often been reserved for the *ortho* isomer.

The number of possible geometrical isomers and enantiomorphic pairs for derivatives of the three $C_2B_{10}H_{12}$ isomers has been determined (345a).

Based on resonance and molecular orbital considerations (17, 316) aromaticlike stability has been predicted for the carboranes. Although thermodynamic data are not yet available, there are now a considerable number of qualitative indications of high chemical stability. 1,2-Dicarba-clovododecaborane(12) is thermally stable up to about 470°C, at which temperature it is converted in good yield into the *meta* isomer, 1,7-dicarba-clovododecaborane(12) (Section III,C,13). The latter compound undergoes extensive decomposition at 630°C, but at 615°C small quantities of *para*-carborane (Section III,C,12) are formed (345). Certain derivatives of carborane (334, 338, 339) survive temperatures up to about 500°C. The fact that the carborane nucleus withstands such treatment contrasts with the behavior of its precursor, decaborane, which undergoes extensive decomposition at about 250°C (346, 347).

Since acetylenic alcohols and acids decompose decaborane, carboranes with $-CH_2OH$ or $-CO_2H$ substituents cannot be prepared directly via Lewis-base-catalyzed reactions between these alkynes and decaborane (325, 330). Nevertheless, indirect formation of derivatives in which $-CH_2OH$ or $-CO_2H$ groups coexist as part of the carborane group (Sections III,C,5,6,7) is again evidence of the stability of the carborane nucleus (330, 334). Furthermore, 1-isopropenylcarborane, when refluxed in methanol, water, or methanol containing hydrochloric acid, is recovered unchanged (326). 1-Isopropenylcarborane also exhibits a remarkable resistance to hot (150°C) 100% sulfuric acid from which it can be recrystallized. Moreover, when this carborane is treated with alkaline permanganate in acetone, the alkenyl group is oxidized but the carborane nucleus remains intact (326, 327). Other oxidizing agents such as chromic acid (334, 337), acyl peroxides, or hypochlorous acid (327) have very little or no effect on the carborane nucleus.

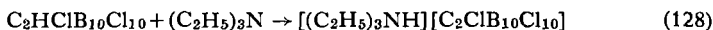
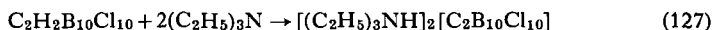
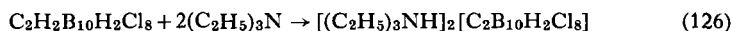
Although $C_2B_{10}H_{12}$ exhibits a remarkable degree of stability for a boron hydride, some chemical degradations have been reported. Degradation of carborane in the presence of methanolic potassium hydroxide (324), or by hydrazine hydrate (327), gives salts of dicarbaundecaborane (Section III, C,10). On the other hand, both hydrazine hydrate and methanolic potassium hydroxide react slowly or not at all with the isomeric neocarborane

(335). Basic permanganate completely degrades 1,2-carboranedicarboxylic acid to boric acid (327).

3. Chlorinated Carboranes

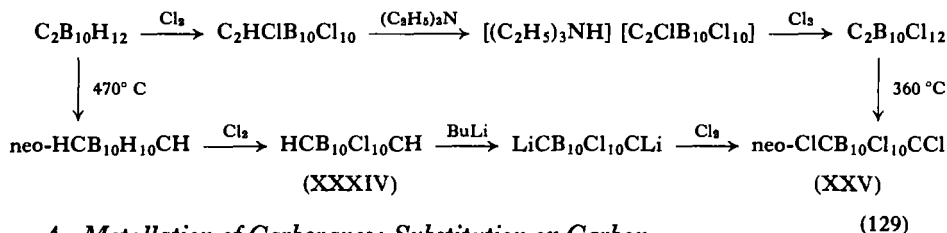
The chlorination of 1,2- $C_2B_{10}H_{12}$ with gaseous chlorine occurs in a step-wise fashion by adjusting the amount of solvent, the reaction time, and, to a lesser degree, the temperature and the use of ultraviolet light. The products isolated in experiments conducted for less than 3 hours are compounds containing two (two isomers), three, four (two isomers), six, eight, and ten chlorine atoms. Ample evidence for *B*-chlorination is provided by both infrared and B^{11} NMR spectral studies (342). Chlorine substitution in the octachloro derivative occurs at B atoms (4, 5, 7, 8, 9, 10, 11, 12) but not at the B atoms (3,6), which are indicated to be the most positively charged by molecular orbital and resonance theories of charge distribution (341). When the carborane chlorination reaction is allowed to proceed for periods of time greater than 3 hours only one additional hydrogen is replaced, affording $C_2HClB_{10}Cl_{10}$ (342). Perchlorination can be accomplished by treating $[(C_2H_5)_3NH][C_2ClB_{10}Cl_{10}]$ (or a corresponding metal salt, Section III,C,4) with chlorine, or by a direct substitution of $C_2HClB_{10}Cl_{10}$ with *N*-chloro-succinimide (344).

Attempts to effect halogen exchange between $C_2H_2B_{10}Cl_{10}$ and Swart's mixture (SbF_3Cl_2), or to promote a reaction between $C_2H_2B_{10}H_4Cl_6$ or $C_2H_2B_{10}H_6Cl_4$ (m.p. $350^\circ C$) and ammonia or amines have been unsuccessful. These results indicate a rather unusual stability for these chlorine-boron bonds. The chlorine atoms, however, are removed at $100^\circ C$ in a 50% aqueous potassium hydroxide-hydrogen peroxide solution (342). Both $C_2H_2B_{10}Cl_{10}$ and $C_2HClB_{10}Cl_{10}$ can be titrated as acids, diprotic and monoprotic respectively, in either ethanol or ethanol-water. Octachlorocarborane, $C_2H_2B_{10}H_2Cl_8$, acts as a diprotic acid only in ethanol-water, whereas carboranes containing six or less chlorine atoms cannot be titrated with hydroxide ion in either ethanol or ethanol-water. The acid strength of the more highly-chlorinated carboranes is further demonstrated by the formation of triethylammonium salts with triethylamine (342)



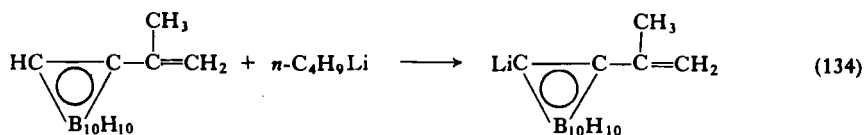
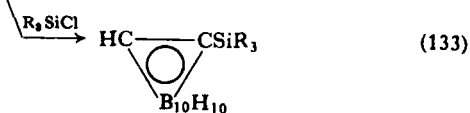
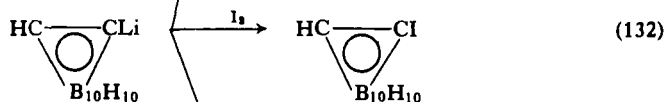
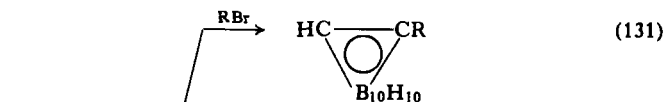
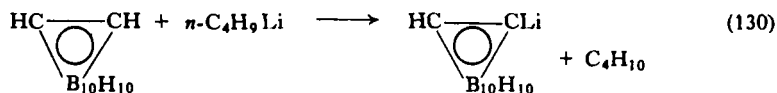
The direct chlorination of neocarborane (Section III,C,13) gives neo- $C_2H_2B_{10}Cl_{10}$ as the ultimate product. As with *ortho*-carborane only B

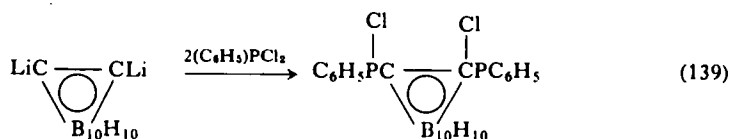
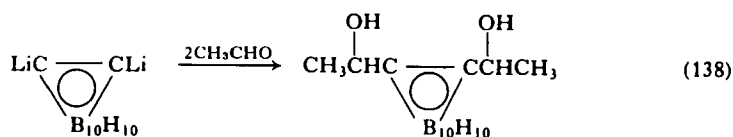
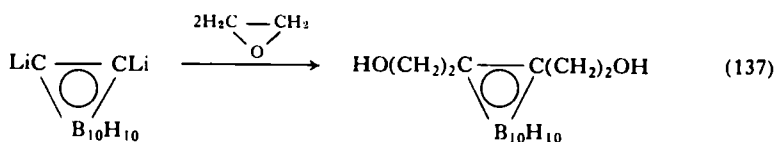
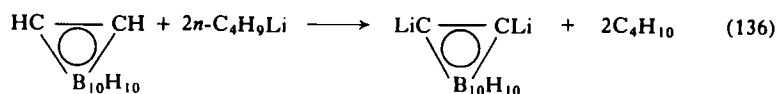
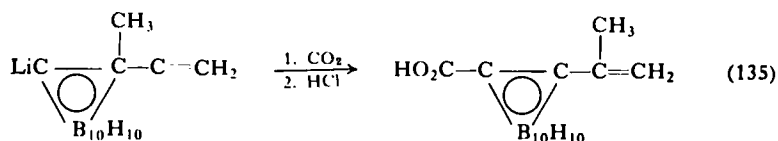
substitution occurs, as indicated by the absence of B—H doublets in the B^{11} NMR (336, 344). Conversion of the decachloroneocarborane (XXXIV) to the metal or ammonium salt, and subsequent reaction with gaseous chlorine affords neo- $C_2B_{10}Cl_{12}$ (XXXV). Consistent with the observed transformation of 1,2- $C_2B_{10}H_{12}$ into neo- $C_2B_{10}H_{12}$ (Section III, C, 2, and 12), the perchlorinated counterpart exhibits an analogous rearrangement at elevated temperatures (344).



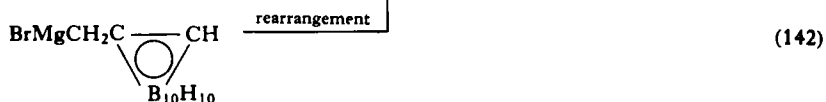
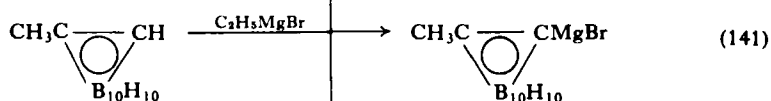
4. Metallation of Carboranes: Substitution on Carbon

The weakly acidic C-hydrogens of carborane react with alkali metal alkyls or amides to produce monosubstituted and disubstituted derivatives [Eqs. (130), (134), and (136)] which in turn undergo many of the reactions common to organometallics (327, 334, 337, 338, 340, 348, 349, 349a, 349b).

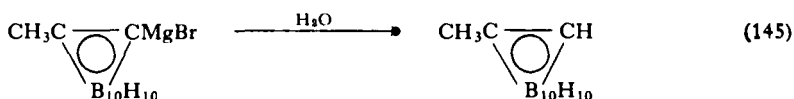
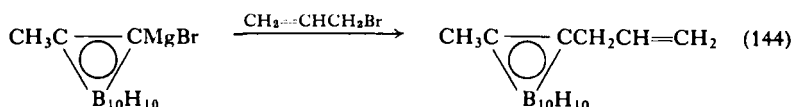
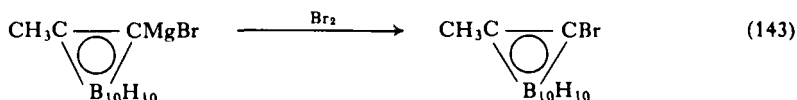




Carboranyl Grignards are prepared using standard procedures [Eqs. (140) and (141)], as well as from a rather interesting rearrangement of 1-carboranyl-methylmagnesium bromide [Eq. (142)] (327, 334).

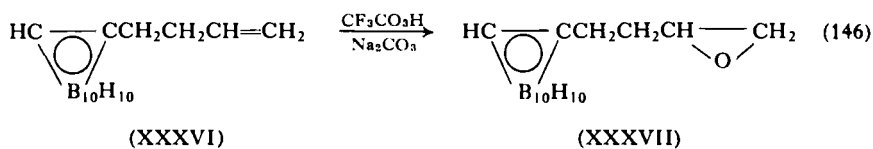


The carboranyl Grignards do not appear to be as generally useful as the lithium derivatives in that they do not react with aldehydes or ketones (334). However, reported reactions with bromine, allyl bromide, or water proceed as might be expected (327, 334).

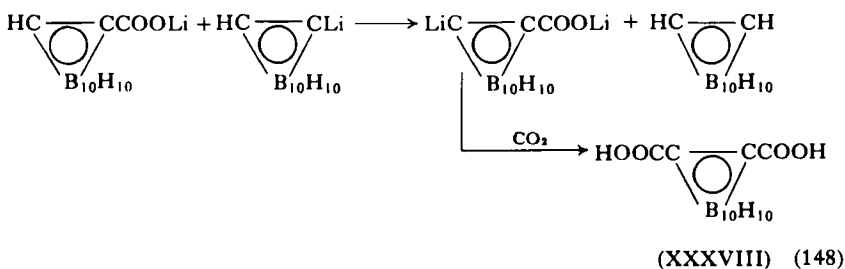


5. Reactions of Alkenylcarboranes: Formation of Epoxides and Diols

Although alkenylcarboranes exhibit the usual olefinic behavior toward catalytic hydrogenation and toward potassium permanganate oxidation, they are quite unreactive to cationic reagents, particularly when the carborane polyhedron and the double bond are separated by a decreasing number of methylene groups (326, 327). Thus bromine adds to the olefinic bond in 4-(1-carboranyl)-1-butene (XXXVI) but does not add to 1-allyl-2-methylcarborane, nor to 1-vinylcarborane. The carborane nucleus also inhibits reactions of neighboring olefinic substituents with hydrogen peroxide, peracetic acid, hypochlorous acid, and iodine monobromide in glacial acetic acid. 1-Isopropenyl-, 1-allyl-, and 1-butenylcarboranes, however, are attacked by trifluoroperacetic acid. Stable epoxides are obtained from isopropenyl- (327) and allylcarborane (334), whereas this peracid converts 4-(1-carboranyl)-1-butene to a glycol trifluoroacetate (327). This difference is attributed to the deactivating influence of the neighboring carboranyl polyhedron on acid-catalyzed ring opening. The epoxide (XXXVII) of the butenylcarborane is obtained from the action of the peracid under alkaline conditions.

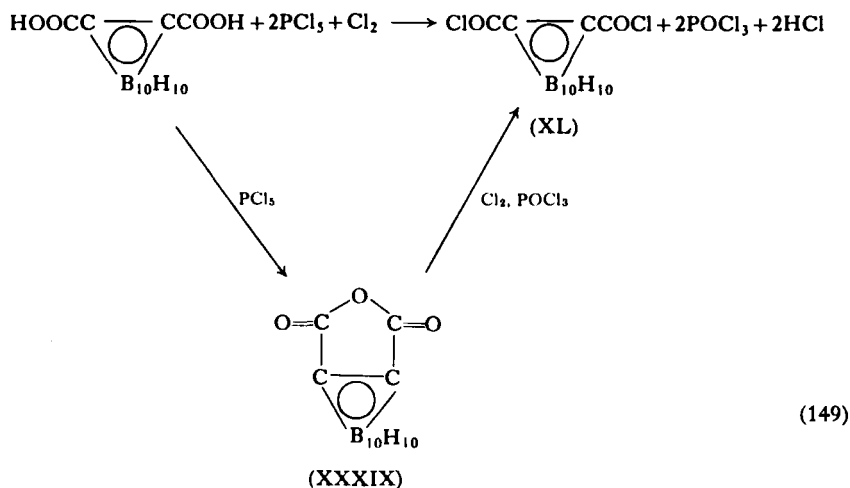


6. Carboxylic Acids and Acid Derivatives

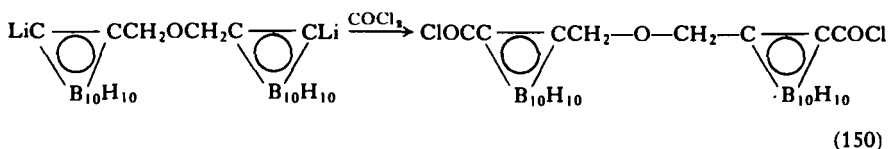
$$\text{HC} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{CH} + n\text{-C}_4\text{H}_9\text{Li} \longrightarrow \text{HC} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{CLi} + \text{C}_4\text{H}_{10} \xrightarrow{\text{CO}_2} \text{HC} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{CCOOLi} \quad (147)$$


In contrast, lithiocarborane reacts with a variety of halides to give monosubstituted carboranes. Carboranecarboxylic acid is obtained by acid hydrolysis of methyl carborane-1-carboxylate (334), which in turn can be directly prepared from decaborane (Section III, C, 1). In comparison, dimethyl 1,2-carboranedicarboxylate cannot be hydrolyzed to the diacid with acidic reagents; and in the presence of aqueous base, hydrolysis occurs only with difficulty and in poor yield, affording the salt of the diacid (XXXVIII) (327). Furthermore, the diester can neither be transesterified nor converted to the diamide via ammonolysis (334). In general, the diacid

and its derivatives exhibit a greater resistance toward nucleophilic reagents than do the monoacid and its derivatives (327, 334, 349). Whereas the monoacid is converted to the acid chloride, and to the amide and ester by commonly accepted procedures, the diacid resists similar conversions. The diacid readily forms a diammonium salt, but attempts to convert the salt to the diamide have been unsuccessful. The anhydride (XXXIX), rather than the diacid dichloride, is obtained by treating the diacid with either thionyl chloride or phosphorus pentachloride. However, the diacid dichloride (XL) can be prepared either by refluxing the anhydride with phosphoryl chloride in a chlorine atmosphere (334), or directly from the diacid by combining the above steps.

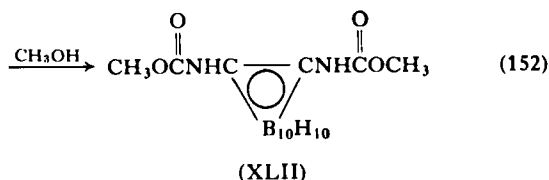
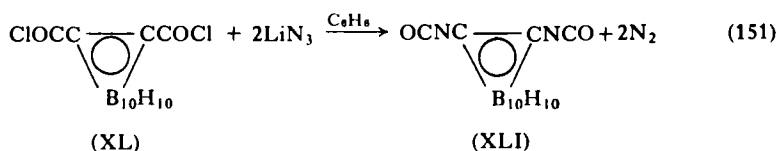


Alternatively, carborane acid chlorides can be prepared from the reaction between lithiocarboranes and phosgene (337).

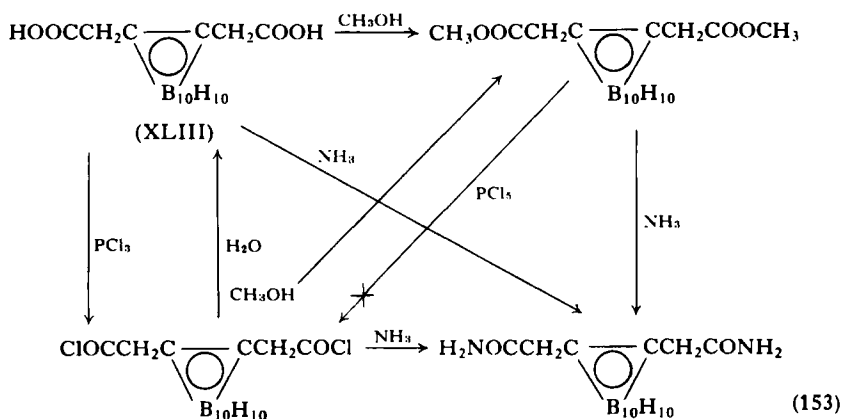


The diacid dichloride (XL) reacts with alcohols to give the diester, which hydrolyzes to the diacid, but in reactions with ammonia or amines no

product has been obtained corresponding to the amide. An unstable diisocyanate (XLI), characterized by its conversion to carborane-1, 2-bis-(methylurethane) (XLII), is formed by the action of lithium azide on (XL) (334).

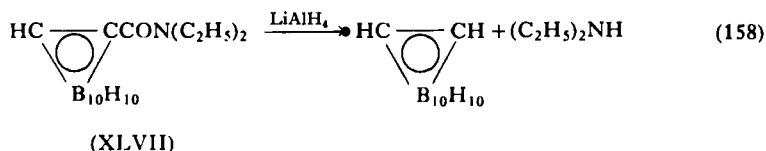


1,2-Bis(carboxymethyl)carborane (XLIII), prepared in good yield by chromic anhydride oxidation of 1,2-bis(β -hydroxyethyl)carborane (Section III, C, 7), undergoes most of the conversions expected of a normal dicarboxylic acid.



A cyclic ketone (XLIV), consistent with Blanc's rule, is formed by heating a mixture of 1,2-bis(carboxymethyl)carborane (XLIII) and barium carbonate under vacuum (334).

Another example of carbon-carbon bond cleavage is to be found in the reduction of the diethylamide of carboranecarboxylic acid (XLVII) with lithium aluminum hydride.

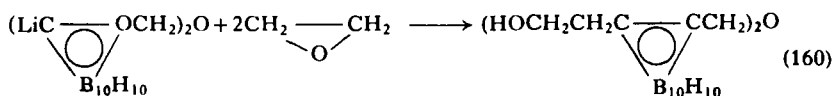
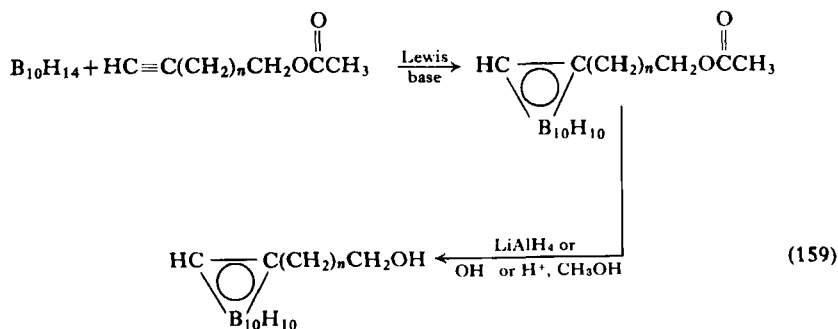


The diethylamide of carboraneacetic acid, on the other hand, is reduced in a normal fashion by lithium aluminum hydride to (β -carboranylethyl)diethylamine (350).

7. Haloalkyls, Alcohols, Ethers

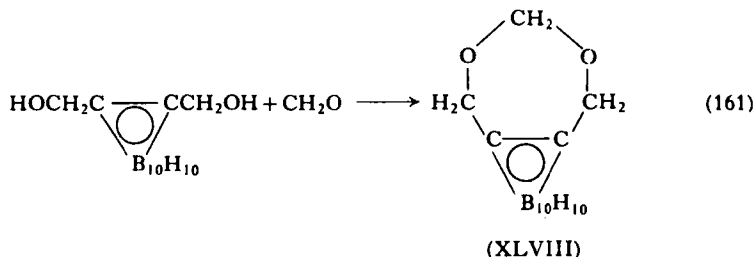
The Grignard derivative of 1-bromomethylcarborane enters into many of the standard reactions, e.g., hydrolysis to produce 1-methylcarborane (327, 330, 334); condensations with ketones (330) and aldehydes (although somewhat sluggish) (334); and displacement reactions with allyl halides, (327, 330), and epoxides (327). Occasionally, the Grignard derivative gives reactions expected for 1-methyl-2-carboranylmagnesium bromide (327, 334), which suggests that a rearrangement has occurred [Eq. (142)].

Displacement of the halogen atom in 1-bromomethylcarborane occurs with difficulty or not at all on treatment with nucleophilic reagents such as iodide ion, sodium diethylmalonate, triethylamine, or hexamethylenetetra-

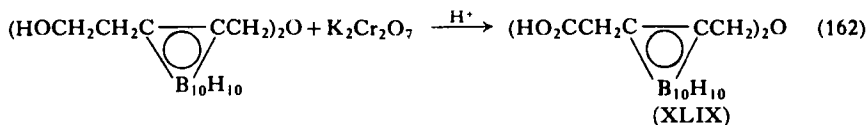


mine (327, 334). The latter reagent forms a B—N adduct with the 1-bromoethylcarborane rather than a quaternary salt (327).

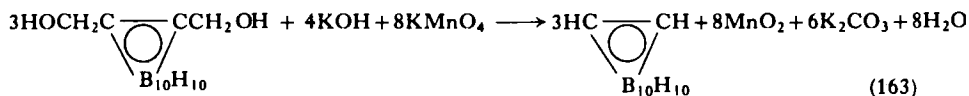
The use of formaldehyde as the carbonyl reagent fails to produce the expected 1,2-bis(hydroxymethyl)carborane from dilithiocarborane (334). It has since been found, however, that formaldehyde readily reacts with this hydroxymethylcarborane to form a cyclic formal (XLVIII) (351).



Chromic acid oxidation of bis(β -hydroxyethyl)carborane proceeds readily, and in good yield, affording the corresponding acid (XLIX) (334, 337).

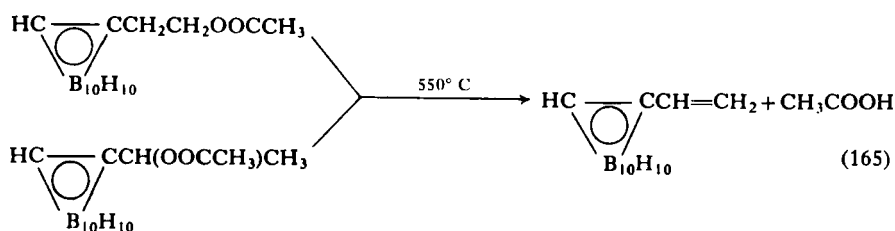
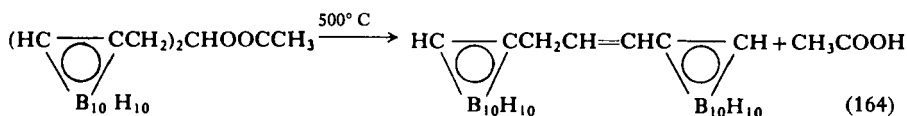


In what appears to be an oxidation followed by a decarboxylation step, the action of aqueous alkaline permanganate on 1,2-bis(hydroxymethyl)carborane (or its diester) provides a convenient route to the parent carborane (327).

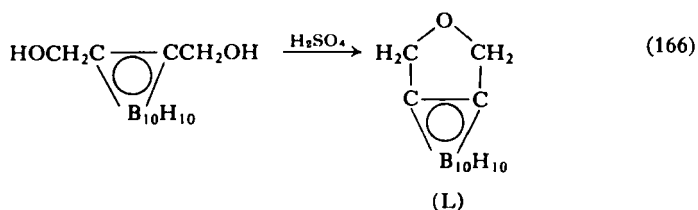


As might be expected, the acetates of a number of hydroxyalkylcarboranes undergo elimination reactions at temperatures of 500° C and above, as illustrated by Eqs. (164) and (165) (334).

A cyclic ether, 1,2-(2'-oxapropylene)carborane (I), is formed by the action of hot, concentrated sulfuric acid on 1,2-bis(hydroxymethyl)carborane (327, 334).



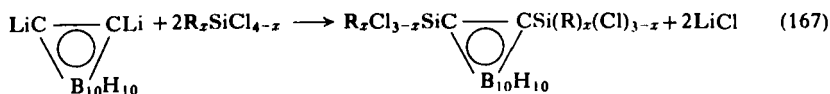
This cyclic ether resists ring opening with Friedel-Crafts type catalysts which are generally useful in opening tetrahydrofuran rings. Halogenation with bromine in sunlight and in the presence of benzoyl peroxide gives a



monobromo derivative in which the bromine atom is attached to a boron rather than a carbon atom (334).

8. Silyl Carboranes

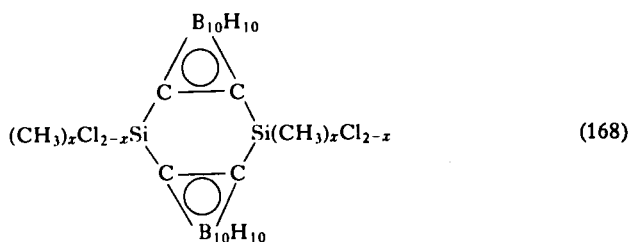
Chlorosilylcarboranes can be prepared by treating dilithiocarboranes with R_2SiCl_2 where R is an alkyl or aryl group. Corresponding tetrachloro and hexachloro derivatives can be made using RSiCl_3 or SiCl_4 (338).



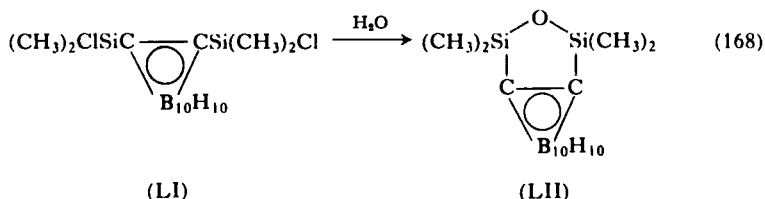
R = alkyl, aryl

x = 0, 1, 2

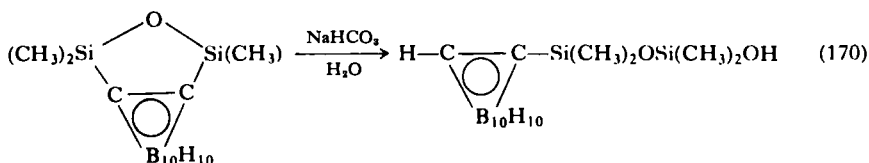
The above silyl carboranes interact further with dilithiocarborane to form products having a six-membered ring incorporating two carborane nuclei.



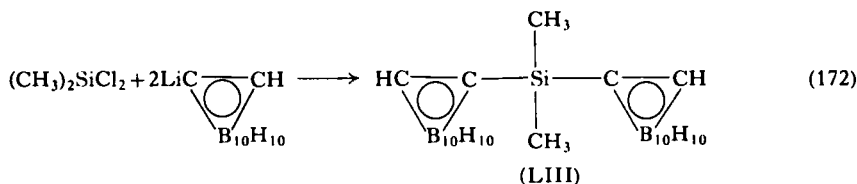
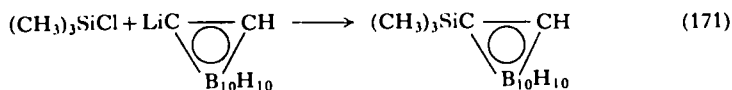
Compound (LI), upon ammonolysis and hydrolysis, yields the exocyclic tetramethyldisilylcarboranyl azane and oxane (LII), respectively (338, 339).



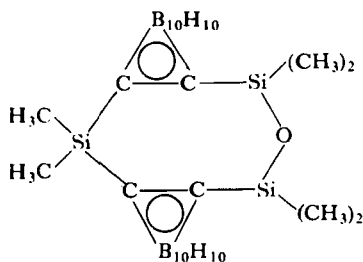
A cleavage of the carboranyl carbon-silicon bond is observed for the latter compound when subjected to a variety of organic and inorganic bases (339).



In contrast to the carboxylation reaction of lithiocarborane (Section III, C, 6), monosilyl derivatives are prepared with little difficulty [Eqs. (171) and (172)] (334).



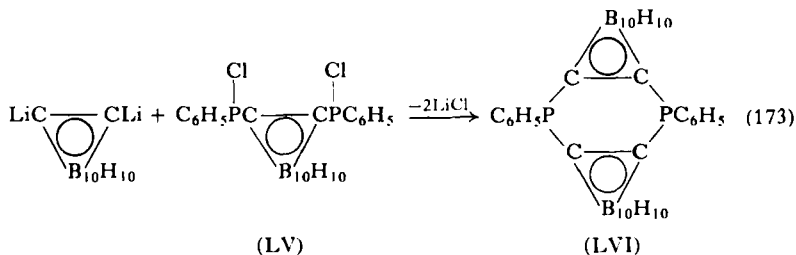
The dilithio derivative of (LIII) reacts with excess of dichlorotetra-methylsiloxane to give (LIV), the first example of two carborane nuclei involved in an eight-membered ring (339).



(LIV)

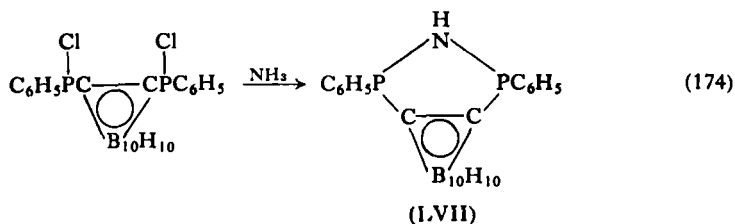
9. Phosphinocarboranes

One molar equivalent of dilithiocarborane reacts with two molar equivalents of either $(\text{C}_6\text{H}_5)_2\text{PCl}$ or $\text{C}_6\text{H}_5\text{PCl}_2$ to form the disubstituted carboranes, $\text{C}_2[\text{P}(\text{C}_6\text{H}_5)_2]_2\text{B}_{10}\text{H}_{10}$ and $\text{C}_2(\text{C}_6\text{H}_5\text{PCl})_2\text{B}_{10}\text{H}_{10}$, respectively. The latter compound 1,2-bis(chlorophenylphosphino)carborane (LV), reacts further with another equivalent of dilithiocarborane to produce a compound (LVI) having two phosphorus atoms and two carborane nuclei in a six-membered ring.

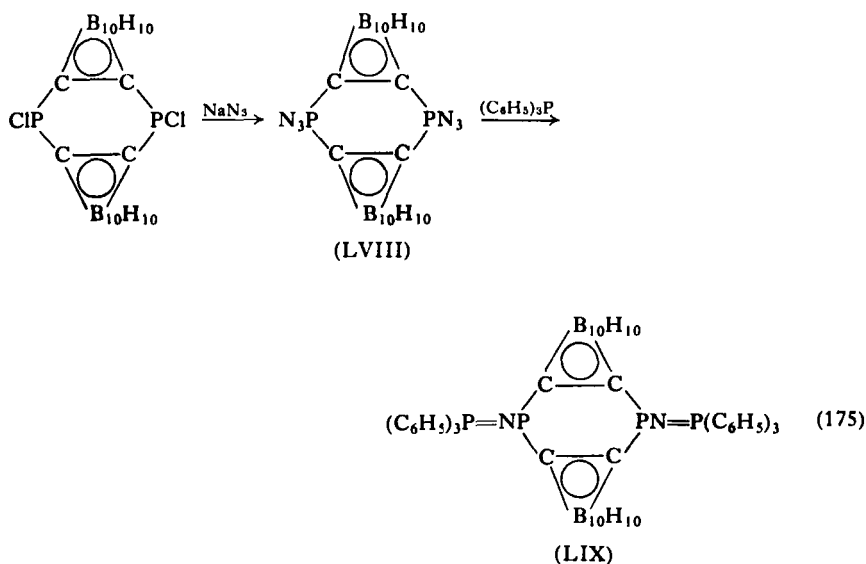


A similar ring structure is assigned to the product $(\text{C}_2\text{PClB}_{10}\text{H}_{10})_2$, obtained by mixing equimolar amounts of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ and PCl_3 .

Treatment of (LV) with sodium azide in ethanol at 0°C gave a bis(azide), $\text{C}_2(\text{C}_6\text{H}_5\text{PN}_3)_2\text{B}_{10}\text{H}_{10}$. A cyclic diphospha(III)azane (LVII) was recovered after an attempt at ammonolysis.

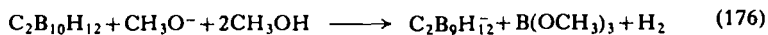


The bis(azide) (LVIII) of the cyclic $(\text{C}_2\text{PClB}_{10}\text{H}_{10})_2$ forms a phosphine-imino derivative (LIX) with triphenylphosphine (340).

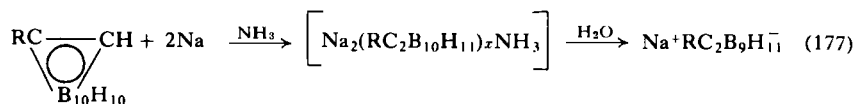


10. Conversion to Dicarbaundecaborane Salts

Both strong caustic solutions (324) [Eq. (176)] and hydrazine hydrate (327) degrade 1,2-dicarbavodecaborane(12) and its *C*-alkyl derivatives to water-soluble salts of dicarbaundecaboranes. The salts may also be prepared



by the hydrolysis of 1:2 carborane-sodium adducts (326, 335).

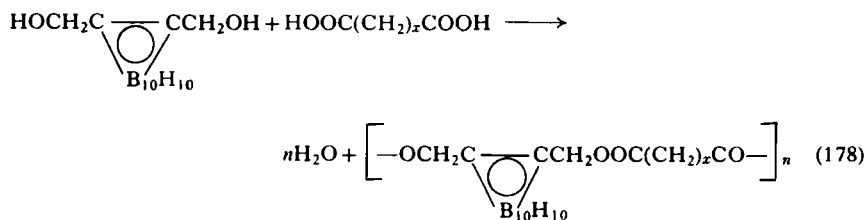


Acidification of the salt with hydrogen chloride produces dicarbaundecaborane(13) (Section III, B, 2). The degradation of *C*-phenylcarborane with hydroxide ion in 50% aqueous ethanol is first order in both hydroxide ion and carborane with a second-order rate constant of $1.48 \pm 0.03 \times 10^{-4}$ liter mole⁻¹ sec⁻¹. A similar reaction of deuterium-labeled *C*-phenylcarborane indicates that the 8, 9, 10, and 12 positions of the carborane icosahedron (XXX) are not involved in the degradation reaction. Since position isomers of the product are not observed, removal of boron atoms in position 3 or 6 is favored (324). A thermal rearrangement of the *C*-phenyldicarbaundecaborate(12) derived from *C*-phenyl-*o*-dicarbaclododecaborane(12) to an isomeric ion prepared directly from the basic degradation of *C*-phenyl-*m*-dicarbaclododecaborane(12) has been recently observed (324b).

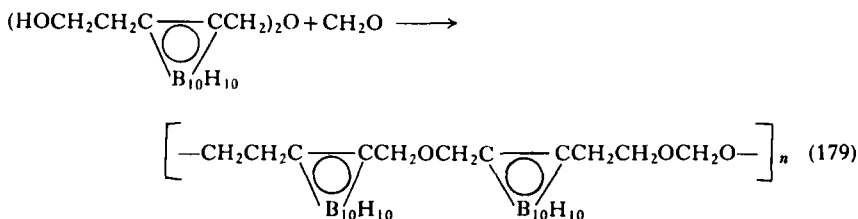
Refluxing methanolic potassium hydroxide does not attack neocarborane (XXXII); and hydrazine hydrate reacts only very slowly with *C*-methylneocarborane, giving a poor yield of water-soluble salt which has not been characterized (335).

11. Carborane Polymers

Polyesters of 2000–20,000 molecular weight are prepared by allowing carborane diols and carborane diacids to react with each other or with organic or fluorocarbon diacids and diols.



Polymers incorporating carboranyl units are also obtained from the reaction between bis(2-hydroxyethyl-1-carboranylmethyl)ether and formaldehyde [Eq. (179)] and from the homopolymerization of carboranylmethylacrylate (351). Other carborane polymers and oligomers have been reported utilizing silyl (351) and phosphinocarborane (340).



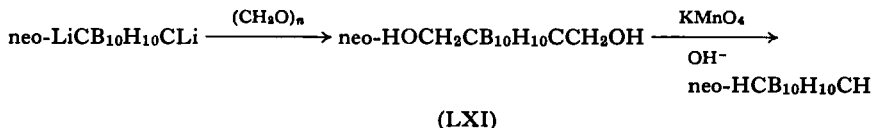
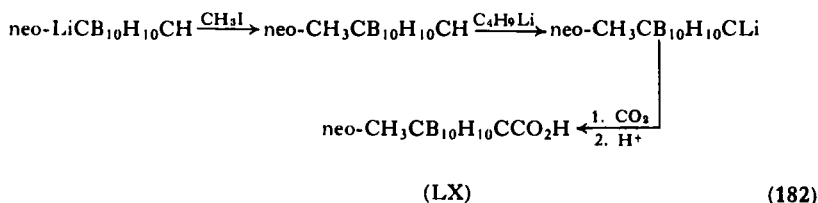
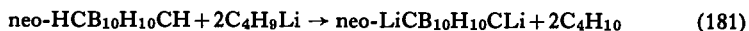
12. Carborane Rearrangements

It has been proposed from bonding principles and molecular orbital theory (309, 311, 316) that 1,7- $\text{C}_2\text{B}_{10}\text{H}_{12}$ (XXXII) should be more stable than 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$ (XXX). The observed rearrangement of carborane (*ortho*) to neocarborane (*meta*) at approximately 470° C (335, 336) is in accord with this prediction. A cube-octahedral intermediate has been suggested for the mechanism of such a rearrangement (318, 352). A consequence of this mechanism is that a further conversion through a cube octahedron to the *para* isomer is not possible. However, *para* isomer (XXXIII) has recently been obtained in low yield from the pyrolysis of neocarborane (345) at 600° C. A cube-octahedral mechanism may still be in operation if, in addition, one of the triangular faces is allowed to rotate 120° at the higher temperature.

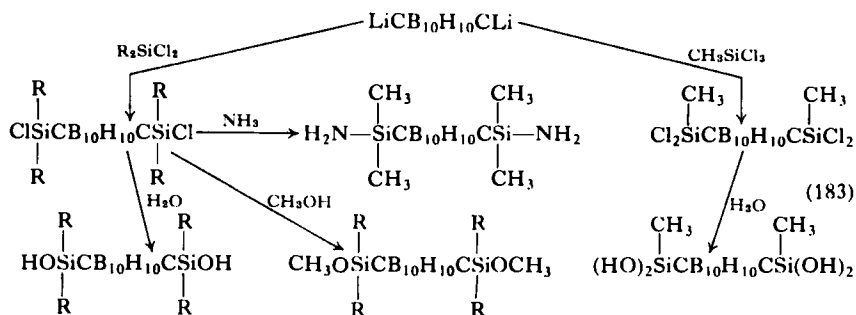
A conversion of neocarborane to carborane occurs via acid hydrolysis of a 1:1 sodium-neocarborane adduct (335). Although a reversal in the *ortho* to *meta* transformation is not expected for the neutral $\text{C}_2\text{B}_{10}\text{H}_{12}$ isomers, an equilibrium situation is, perhaps, more accessible in the corresponding ions (318). A kinetically controlled hydrolysis of the ion may then favor the *ortho* isomer of $\text{C}_2\text{B}_{10}\text{H}_{12}$.

From the geometry of neocarborane one would not expect the *meta* carbons to participate in a small exocyclic ring, and thus far, no such examples have been reported. Participation of the *ortho* isomer, 1,2- $\text{C}_2\text{B}_{10}\text{H}_{12}$, in five and six-membered rings is well established (327, 334, 337–340). Although the carbon atoms in the icosahedron should, upon heating, show a tendency to rearrange to the neocarborane structure, the exocyclic derivatives should resist such a rearrangement. Generally, such exocyclic 1,2-carboranes are stable up to 500°–600° C at which temperature severe decomposition occurs (339). On the other hand, 1,2-carborane derivatives with no such restrictive attachments are easily rearranged when subjected to “normal” rearrangement conditions (section III, C, 3) (335).

As with carborane, neocarborane undergoes facile stepwise metallation with lithium alkyls to give the synthetically useful *C*-lithio- and *C,C'*-dilithionecarboranes.



Ammonolysis of the diacid chloride, obtained from the treatment of *C,C'*-neocarboranecarboxylic acid with phosphorus pentachloride, gives the diacid amide. Pyrolysis of the latter compound does not result in the formation of a cyclic imide, as is observed in the corresponding 1,2- $C_2B_{10}H_{12}$ derivative (Section III, C, 6) (335). A number of silyl derivatives have been prepared from dilithioneocarborane, and again, in contrast to the isomeric silylcarboranes (Section III, C, 8), they do not tend to form exocyclic derivatives (353). These observations are consistent with the 1,7-arrangement of the carbons in the neocarborane icosahedron.



R = $-\text{CH}_3$, $-\text{C}_6\text{H}_5$

The chlorinated derivatives of neocarborane are discussed in Section III, C, 3.

14. Nuclear Magnetic Resonance

The B^{11} NMR spectra have provided a useful physical method for expeditious structural studies on the isomeric carboranes. Theoretical spectra have been deduced for the geometrical isomers of the icosahedral $\text{C}_2\text{H}_2\text{B}_{10}\text{H}_{10}$ (Fig. 14) by grouping the boron atoms on the basis of their affiliation with

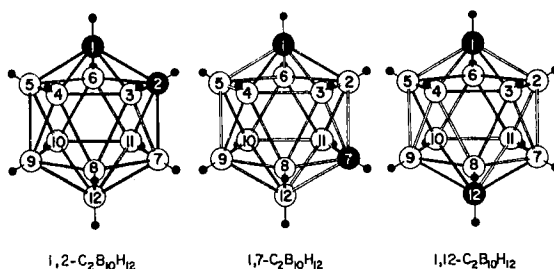


FIG. 14. Geometrical isomers of $\text{C}_2\text{B}_{10}\text{H}_{12}$.

one or both of the carbon atoms (336). The spectrum of the *para* isomer (1,12) should consist of only one doublet (H coupled to B), for all of the boron atoms are geometrically equivalent. The low-melting isomer (m.p. $259^\circ\text{--}261^\circ\text{C}$) (345) satisfies this requirement. The *meta* isomer (1,7) has "three" (336) kinds of boron atoms, two of them (2,3) are affiliated with both carbons, six of them with only one carbon, and the remaining two (9,10) have no carbon in their immediate environment. On this basis the spectrum should display three doublets, with an intensity ratio of 2:6:2. This pattern has been

observed for neocarborane (m.p. 272° – 273° C) which is thus assigned the *meta* configuration. For the *ortho* isomer there are two boron atoms (3,6) affiliated with both carbon atoms, four (4, 5, 7, 11) are adjacent to one or the other carbon, and four (8, 9, 10, 12) have only boron atoms in their immediate environment. The observed spectrum for the remaining isomer (m.p. 294° – 296° C) obtained from the alkyne–decaborane reaction (Section III, C, 1), consists of two doublets with an area of 2:8. This requires coincidental overlap of the doublets expected for boron atoms 4, 5, 7, 8, 9, 10, 11, 12. Since the boron resonances are not extremely sharp this coincidence is not particularly disturbing (336).


On closer examination of the *ortho* and *meta* isomers of the icosahedral dicarbaclovododecaborane it is, to some degree, fortuitous that the correct structural assignments are made on the basis of B^{11} NMR. Geometrically, there are four groups of boron atoms for both isomers in a ratio 2:4:2:2. The groups are: (1) for the *ortho* isomer, (a) boron atoms 3, 6; (b) 4,5,7,11; (c) 8,10; (d) 9,12; and (2) for the *meta* isomer, (a) boron atoms 2,3; (b) 4,6,8,11; (c) 5,12; and (d) 9,10. By invoking the proper coincidental overlapping it is possible to predict that either isomer, *ortho* or *meta*, could give either of the observed resonance intensity ratios [i.e., 2:6:2 or 2:8 (336, 342)]. In highly delocalized systems, such as the carboranes, long-range chemical shift effects are not to be discounted. Such long-range effects could, but apparently do not, refute assignments based primarily upon the number of directly attached or neighboring carbon atoms. Recently, a B^{11} NMR spectrum at 60 Mc has been taken and reveals all four sets of doublets for the *ortho* isomer of $C_2B_{10}H_{12}$ (353a).

Only a very limited number of H^1 NMR spectra of carborane derivatives have been reported (339, 342).

15. *Electron-Withdrawing Characteristics of the Carborane Nucleus*

A correlation of the Si—O—Si infrared band in an exocyclic carboranyl-siloxane with other substituted siloxanes indicates a Taft polar-substituent constant, σ^* of about 3.0–3.5 for the 1,2-dicarbaclovododecaborane(12) group (354). This places the electron-withdrawing character of the carboranyl group in the vicinity of other strong electron-withdrawing groups, e.g., $-Cl$, $-F$, and $-CN$ with σ^* values of 2.94, 3.08, and 3.64, respectively. Acid strengths for 1-methyl-2-carboranecarboxylic acid, $pK_a = 2.8$ (335, 355), and 1-methyl-7-neocarboranecarboxylic acid, $pK_a = 3.1$ (335) are in qualitative agreement with this assignment. Some chemical evidence is

TABLE VIII
C₂B₁₀H₁₂ DERIVATIVES

Compound		Physical properties			
		References	M.p. (°C)	B.p. (°C/mm)	Other
<i>1,2-Dicarbaclododecaborane Derivatives</i>					
					
R	R'				
H	H	325	320°	—	IR (335, 340, 342)
		326	285°–287°	—	B ¹¹ NMR (336, 342)
		345	294°–296°	—	MS (335)
		327	287°–288°	—	—
		343	294°	—	—
H	CH ₃	325	114°–115°	—	—
		326	214°–215°	—	—
		330	214°–217°	—	—
		327	218°–219°	—	—
H	CH ₂ CH ₃	330	—	75°–80°/0.5	—
H	CH ₂ CH ₂ CH ₃	330	68°–69°	—	—
		325	62°	—	—
H	CH(CH ₃) ₂	326	–4°	100°/4	n _D ²⁵ 1.5395 d ₄ ²⁵ 0.926 IR, UV

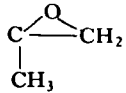
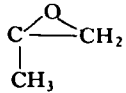
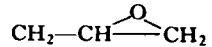
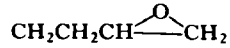
H	$\text{CH}_2(\text{CH}_2)_2\text{CH}_3$	325	—	75°/0.1	n_D^{25} 1.5301
H	$\text{CH}_2(\text{CH}_2)_4\text{CH}_3$	330	—	101°–102°/0.5	n_D^{25} 1.5211 (330)
		325	—	101°–102°/0.5	
H	$\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	325	33°	—	—
H	C_6H_5	325	66°–67°	—	—
		330	69.5°–70°	—	—
H	$\text{CH}=\text{CH}_2$	330	76°–77°	75°–77°/0.5	—
		325	78°–79°	75°–80°/0.5	—
		334	76°–77°	—	—
H	$\text{C}(\text{CH}_3)=\text{CH}_2$	325	45°–46°	—	—
		326	46.7°–47–7°	50°/1.6	d_4^{25} 0.942
					n_D^{50} 1.5432, UV, IR
H	$\text{CH}_2\text{CH}=\text{CH}_2$	334	63°–65°	—	—
H	$\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	327	45°–46°	99°–101°/0.2	—
H	$\text{C}\equiv\text{CH}$	332	75°–78°	—	—
		326	—	96°–100°/0.3	IR, n_D^{25} 1.5483
H					
H	$\text{CH}_2-\text{CH}-\text{CH}_2$ 	334	68°	—	—
H	$\text{CH}_2\text{CH}_2\text{CH}-\text{CH}_2$ 	327	60°–62°	132°–135°/0.4	—
H	CH_2OH	330	220°–222°	—	—
		334	225°	—	—
H	CH_2Cl	330	83°–85°	—	—
H	CH_2Br	326	47°–49°	—	—
		325	30°	—	—

TABLE VIII—continued

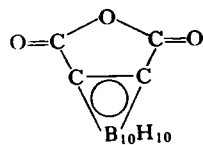
Physical properties					
	Compound	References	M.p. (° C)	B.p. (° C/mm)	Other
H	CH ₂ CH ₂ Cl	330	80°–82°	—	—
H	CH ₂ CH ₂ Br	330	114°–115°	—	—
H	CH ₂ CH ₂ CH ₂ Cl	330	53°–55°	—	—
H	CH ₂ CH ₂ CH(OH)CH ₂ Cl	327	—	135°–145°/0.1	—
H	CH ₂ CH(OH)CH ₂ OH (2 forms)	334	89°–90°	—	—
H	COOH	334	150°	—	—
		348	150°–150.5°	—	—
H	COOCH ₃	325	73°	—	—
H	COOC ₂ H ₅	350	61°–62°	—	—
H	CONHC ₆ H ₅	334	132°–133°	—	—
H	CON(C ₂ H ₅) ₂	350	109°	—	—
H	CH ₂ CON(C ₂ H ₅) ₂	350	82°–83°	—	—
H	CH ₂ CH ₂ COOH	350	147°–149°	—	—
H	(?)CH ₂ CH(CO ₂ H) ₂	327	146°–147°	—	—
H	CH ₂ CH(CO ₂ CH ₂ CH ₃) ₂	330	—	144°–148°/0.2	—
H	CH ₂ C(CH ₃)(CO ₂ CH ₂ CH ₃) ₂	330	—	164°/0.5	n_D^{25} 1.5131
H	CH ₂ N(C ₂ H ₅) ₂	325	33°–35°	—	—
H	CH ₂ CH ₂ N(C ₂ H ₅) ₂	350	46.5°–48°	—	—
H	CH ₂ OOCCH ₃	325	42°–43°	82°–84°/0.2	—
		330	48°–48.5°	110°/0.5	—
H	CH(CH ₃)OOCCH ₃	325	—	85°–95°/0.2	n_D^{21} 1.5291
H	CH ₂ OOCCH=CH ₂	330	—	98°–100°/0.2	n_D^{25} 1.5390
H	CH ₂ CH ₂ OOCCH ₃	325	61°–63°	146°/1.6	—

H	CH ₂ CH(CH ₂ OOCCH ₃) ₂	330	—	180°–184°/0.4	—
H	I	327	131°–136°	—	—
H	Si(CH ₃) ₃	334	94°–95°	—	—
H	Si(C ₆ H ₅) ₃	334	165°–167°	—	—
H	CH ₂ Si(CH ₃) ₃	334	52°	—	—
H	Si(CH ₃) ₂ OSi(CH ₃) ₂ OH	339	—	—	IR, H ¹ NMR
CH ₃	CH ₂ CH=CH ₃	327	17°–18°	—	—
CH ₃	CH ₂ Br	330	125°–127°	—	—
CH ₃	COOH	335	201°–203°	—	—
		348	194°–195°	—	—
CH(CH ₃) ₂	COOH	348	160°–161°	—	—
C ₄ H ₉	COOH	348	87°–88°	—	—
CH ₂ OH	CH ₂ OH	330	—	—	—
		334	303°–304°	—	—
CH ₂ OH	C≡C—CH ₂ OH	330	163°–164°	—	—
CH ₂ OH	COOH	337	—	—	IR
CH ₂ Cl	CH ₂ Cl	330	114°–115°	—	—
		343	114°–115°	—	—
		325	119°–120°	—	—
CH ₂ Br	CH ₂ Br	326	68°–69.5°	—	—
		343	66°	—	—
COOH	COOH	334	232°	—	—
		348	216°–217°	—	—
		327	225°	—	—
COOH	CH=CH ₂	348	142.5°–143°	—	—
COOH	C(CH ₃)=CH ₂	334	175°	—	—
COCl	COCl	334	69°–70°	—	—
COOCH ₃	COOCH ₃	325	66°–67°	—	—
		330	52°–54°	108°/0.5	—
COOC ₂ H ₅	COOC ₂ H ₅	350	10°–11°	—	—

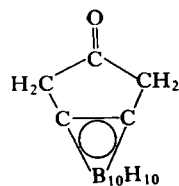
TABLE VIII—*continued*

		Physical properties			
Compound		References	M.p. (° C)	B.p. (° C/mm)	Other
CH ₂ OOCCH ₃	CH ₂ OOCCH ₃	325	43°–44°	—	—
		326	42°–43°	—	—
CH ₂ OOCCH ₃	C≡CCH ₂ OOCCH ₃	330	—	—	—
CH ₂ OOCCH ₃	C≡CCH ₂ OOCCH ₂ CH ₃	330	250°	—	—
CH(OH)CH ₃	CH(OH)CH ₃	334	> 400°	—	—
CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	334	125°	—	—
		327	124°–125°	—	—
CH ₂ COOH	CH ₂ COOH	334	203°–205°	—	—
CH ₂ COOCH ₃	CH ₂ COOCH ₃	334	47°–48°	—	—
CH ₂ COOCH ₂ CH ₃	CH ₂ COOCH ₂ CH ₃	334	40°	—	—
CH ₂ COCl	CH ₂ COCl	334	—	—	—
CH ₂ CH ₂ CH ₃	Br	325	44°–45°	107°/1	—
CH(CH ₃) ₂	CH(CH ₃) ₂	330	104°–105°	—	—
CH ₂ (CH ₂) ₂ CH ₃	Br	325	—	85°–90°/0.5	n_D^{25} 1.5500
C(CH ₃)=CH ₂	C(CH ₃)=CH ₂	330	82°–83°	—	—
C ₆ H ₅	C ₆ H ₅	326	148°–149°	—	—
C ₆ H ₅	COOH	348	142°–143°	—	—
NCO	NCO	334	—	—	IR
NHCO ₂ CH ₃	NHCO ₂ CH ₃	334	257°–258°	—	—
P(C ₆ H ₅) ₂	P(C ₆ H ₅) ₂	340	219°	—	—
P(C ₆ H ₅)Cl	P(C ₆ H ₅)Cl	340	172°–174°	—	—
P(C ₆ H ₅)N ₃	P(C ₆ H ₅)N ₃	340	126°–128°	—	—

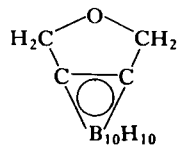
SiCl ₃	SiCl ₃	338	121°–122°	—	—
Si(CH ₃) ₂ Cl	Si(CH ₃) ₂ Cl	338	112.5°–113.5°	—	—
Si(C ₆ H ₅) ₂ Cl	Si(C ₆ H ₅) ₂ Cl	338	244°–245°	—	—
Si(CH ₃)Cl ₂	Si(CH ₃)Cl ₂	338	119°–120°	—	—
Li	Li	340	—	—	—

Cyclic Compounds

334	180°	—	—
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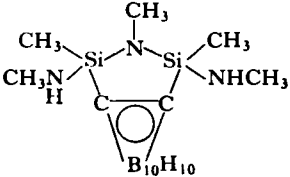
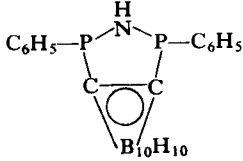
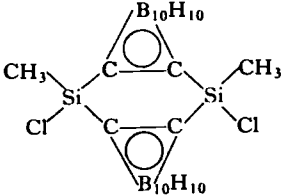


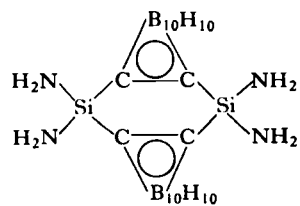
334	170°	—	—
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334	259.5°–260.5°	—	IR
327			

TABLE VIII—*continued*

Compound	Physical properties			
	References	M.p. (° C)	B.p. (° C/mm)	Other
	338	128°–129.5°	—	—
	340	222°–224°	—	—
<i>Cyclic Compounds</i>				
	339	281°–283°	—	—

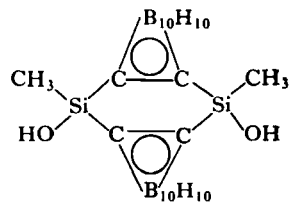


339

347°–349°

—

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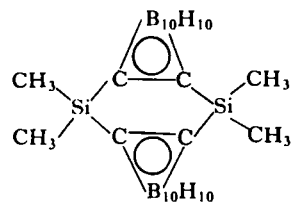


339

304°

—

—

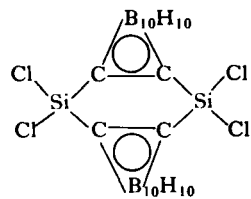


338

309°–310°

—

—



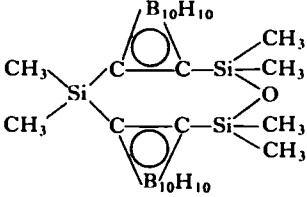
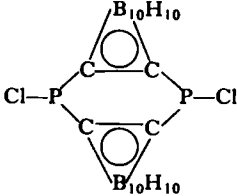
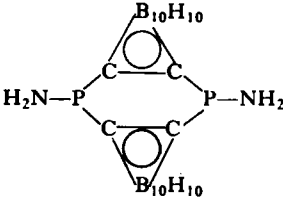
339

271°–272°

—

—

TABLE VIII—continued

Compound	Physical properties			
	References	M.p. (° C)	B.p. (° C/mm)	Other
	339	207°–208°	—	—
	340	240°–241°	—	IR
	340	280°	—	IR

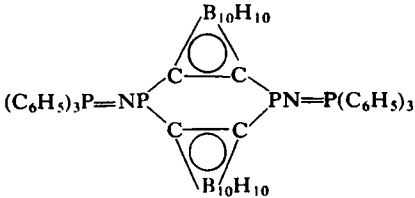
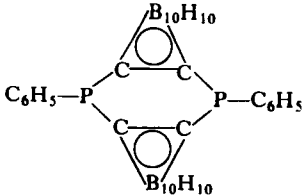
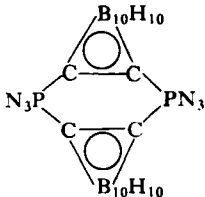
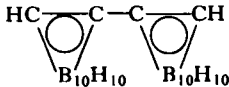
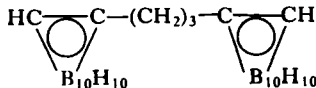
	340	311°–312°	—	—
	340	356°–358°	—	—
	340	150° (dec)	—	—
<hr/>				
<i>Compounds with Two Carboranyl Units</i>				
	332	309°–310°	—	—
	325	355°–357°	—	—
	326	346°–348°	—	—

TABLE VIII—continued

Compound	Physical properties			
	References	M.p. (° C)	B.p. (° C/mm)	Other
$\left(\begin{array}{c} \text{HC} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{C}(\text{CO}_2\text{CH}_2\text{CH}_3)_2$	330	198°–199°	—	—
$\left(\begin{array}{c} \text{HC} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{CHOOCCH}_3$	334	206°–207.5°	—	—
$\begin{array}{c} \text{HC} \text{---} \text{CCH}_2 \text{---} \text{CH}=\text{CH} \text{---} \text{C} \text{---} \text{CH} \\ \diagup \quad \diagdown \qquad \qquad \diagdown \quad \diagup \\ \text{B}_{10}\text{H}_{10} \qquad \qquad \text{B}_{10}\text{H}_{10} \end{array}$	334	> 300°	—	—
$\left(\begin{array}{c} \text{HC} \text{---} \text{C} \text{---} \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{Si}(\text{CH}_3)_2$	334	195°–196.5°	—	—
$\left(\begin{array}{c} \text{HC} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{C}(\text{COOH})_2$	327	65°–70° (dec)	—	—
$\left(\begin{array}{c} \text{HC} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{O}$	337	342°–344.5°	—	IR

$\left(\begin{array}{c} \text{HC} \text{---} \text{CCH}_2\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{O}$	337	117°–118°	—	—
$\left(\begin{array}{c} \text{HO}_2\text{CC} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{O}$	337	235°	—	IR
$\text{H} \text{---} \begin{array}{c} \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \text{CCH}_2\text{OCH}_2\text{C} \text{---} \begin{array}{c} \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \text{CCO}_2\text{H}$	337	73°	—	—
$\left(\begin{array}{c} \text{ClOCC} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{O}$	337	86°–89°	—	—
$\left(\begin{array}{c} \text{HOCH}_2\text{C} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{O}$	337	> 350°	—	IR
$\left(\begin{array}{c} \text{HOCH}_2\text{CH}_2\text{C} \text{---} \text{C} \text{---} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{O}$	337	126°–128°	—	—
$\left(\begin{array}{c} \text{HO}_2\text{CCH}_2\text{C} \text{---} \text{CCH}_2 \\ \diagup \quad \diagdown \\ \text{B}_{10}\text{H}_{10} \end{array} \right)_2 \text{O}$	337	242°–244°	—	—

TABLE VIII—continued

Compound	Physical properties			
	References	M.p. (°C)	B.p. (°C/mm)	Other
<i>Carborane Adducts</i>				
[HN(C ₂ H ₅) ₃] ₂ (C ₂ B ₁₀ Cl ₁₀)	342	200°–201°	—	—
[HN(C ₂ H ₅) ₃] ₂ (C ₂ B ₁₀ H ₂ Cl ₈)	342	185°–187°	—	—
[HN(C ₂ H ₅) ₃](C ₂ ClB ₁₀ Cl ₁₀)	342	166°	—	—
[(C ₆ H ₅) ₃ PCH ₃] ₂ C ₂ ClB ₁₀ Cl ₁₀	342	182°	—	—
[Piperidine] ₂ C ₂ H ₂ B ₁₀ H ₁₀	327	171°–176°	—	IR
[Isopropylamine] ₂ C ₂ H ₂ B ₁₀ H ₁₀	327	110°–115°	—	—
<i>Boron-Substituted Carboranes</i>				
C ₂ H ₂ B ₁₀ H ₉ CH ₂ CH ₃ (<i>B</i> -ethylcarborane)	325	—	70°/0.3	<i>n</i> _D ²⁵ 1.5375
C ₂ H ₂ B ₁₀ H ₈ Cl ₂	342	232°	—	—
C ₂ H ₂ B ₁₀ H ₈ Cl ₂	342	250°–252°	—	—
C ₂ H ₂ B ₁₀ H ₇ Cl ₃	342	241°–243°	—	—
C ₂ H ₂ B ₁₀ H ₆ Cl ₄	342	250°	—	—
C ₂ H ₂ B ₁₀ H ₆ Cl ₄	342	351°	—	—
C ₂ H ₂ B ₁₀ H ₄ Cl ₆	342	306°	—	—
C ₂ H ₂ B ₁₀ H ₂ Cl ₈	342	272°	—	—
C ₂ H ₂ B ₁₀ Cl ₁₀	342	259°	—	H ¹ and B ¹¹ NMR B ¹¹ NMR (344)
C ₂ HClB ₁₀ Cl ₁₀	342	279°	—	H ¹ and B ¹¹ NMR
C ₂ Cl ₂ B ₁₀ Cl ₁₀ (C ₂ B ₁₀ Cl ₁₂)	344	448°	—	IR, B ¹¹ NMR
C ₂ (CH ₃)HB ₁₀ Cl ₁₀	344	—	—	B ¹¹ NMR

$C_2(C_2H_5)HB_{10}Cl_{10}$	344	—	—	B^{11} NMR
$C_2(CH_3)_2B_{10}Cl_{10}$	344	—	—	B^{11} NMR
$C_2(C_2H_5)_2B_{10}Cl_{10}$	344	—	—	B^{11} NMR

1,7-Dicarbaclovododecaborane (Neocarborane) Derivatives

R	R'				
H	H	336	265° (353) 272°–273° (345)	—	B^{11} NMR (336)
		335	263.5°–265°	—	MS, IR (335)
H	CH ₃	335	208°–210°	—	—
CH ₃	COOH	334	108°–111°	—	—
CH ₂ OH	CH ₂ OH	335	194°–196°	—	—
COOCH ₃	COOCH ₃	335	52.5°–54°	—	—
COOH	COOH	335	202°–204°	—	—
Si(CH ₃) ₂ Cl	Si(CH ₃) ₂ Cl	353	—	102°–104°/0.1	—
Si(C ₆ H ₅) ₂ Cl	Si(C ₆ H ₅) ₂ Cl	353	131°–133°	—	—
Si(CH ₃)Cl ₂	Si(CH ₃)Cl ₂	353	—	103°–105°/0.15	—
Si(CH ₃) ₂ OH	Si(CH ₃) ₂ OH	353	98°–99.5°	—	—
Si(CH ₃) ₂ NH ₂	Si(CH ₃) ₂ NH ₂	353	41.5°–43.5°	—	—
Si(CH ₃) ₂ OCH ₃	Si(CH ₃) ₂ OCH ₃	353	36°–37°	108°–110°/0.1	—
Si(CH ₃)(OH) ₂	Si(CH ₃)(OH) ₂	353	136.5°–138.5°	—	—
Si(C ₆ H ₅) ₂ OH	Si(C ₆ H ₅) ₂ OH	353	153°–155°	—	—
Si(C ₆ H ₅) ₂ OCH ₃	Si(C ₆ H ₅) ₂ OCH ₃	353	151°–153°	—	—

Boron-Substituted Neocarboranes

$C_2H_2B_{10}Cl_{10}$	336	235°	—	B^{11} NMR
	344			
$C_2B_{10}Cl_{12}$	344	443°	—	IR, B^{11} NMR

1,12-Dicarbaclovododecaborane (para-Carborane)

$C_2H_2B_{10}H_{10}$	345	259°–261°	—	IR, B^{11} NMR
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available to support the strong electron-withdrawing character of the carborane nucleus (326, 327, 339); however, the issue is clouded, in some respect, by other undetermined factors (327, 334).

Known derivatives of the *ortho*, *meta*, and *para* isomers of $C_2B_{10}H_{12}$ are summarized in Table VIII.

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The Structures of Organolithium Compounds

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I

INTRODUCTION

Organolithium compounds have been employed in synthetic work for many years, but their physical properties and structures have come under intensive study only recently. This review summarizes the evidence relating to the structures of organolithium and related compounds, and describes structural models which are consistent with both experimental and theoretical evidence. The implications of structural considerations for an understanding of the mechanisms of organolithium reactions are also discussed.

A. Electron Deficiency

The organolithium compounds are members of a larger class which is often referred to as *electron deficient*, and which includes Group II and III

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organometallic compounds, boron hydrides, and others (1-3). Electron deficiency is characterized by the formation of polymeric species through delocalization of one or more bonding electron pairs. Thus, diborane arises from association of two BH_3 units to form B_2H_6 , with delocalization of two bonding electron pairs into two three-center bridge orbitals. The appearance—at least in a formal sense—of multicenter bonds such as the B—H—B bridge in diborane, or the Al—C—Al bridge in $\text{Al}_2(\text{CH}_3)_6$, is a concomitant feature of electron-deficient bonding.

Electron deficiency in a topological sense (2) refers to molecular structures in which the number of nearest-neighbor atom-atom connections (i.e., bonds) exceeds the number of valence electron pairs. Thus, again in B_2H_6 , the nearest-neighbor connections are eight in number (nine if the B—B connection is included), whereas there are but six valence shell electron pairs, available for bonding. The criteria for determination of what constitutes a valid atom-atom connection are not always unambiguous, but reference to a bond order-bond length relationship such as Pauling's (4) is generally satisfactory as an approximate basis.

The electronic structural consequences of electron deficiency are thoroughly discussed in many places (1-3). We defer a consideration of organolithium electronic structures until some of the experimental data have been presented.

B. Preparation and Properties

Organolithium compounds vary widely in reactivity, but all are vigorously reactive with both air and moisture. The pure solids ignite instantly on contact with air. All preparative work and subsequent isolation and handling of the pure substances must therefore be performed under an inert atmosphere, usually argon or nitrogen, or in a vacuum system.

For most purposes of structural studies it is desirable to obtain a purified compound free from other reaction products or other impurities accumulated during the preparation. Solids which are sufficiently soluble in hydrocarbon solvents to permit recrystallization are therefore most desirable. The first isolation of organolithium compounds was effected by Schlenk and Holtz in 1917 (5). Their method of preparation involved a metal-metal interchange with alkylmercury compounds, e.g.,

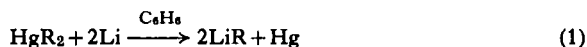
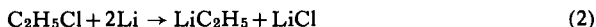


TABLE I
PHYSICAL PROPERTIES OF ORGANOLITHIUM COMPOUNDS

Compound	M.p. (° C)	Solubility in hydrocarbons	Comments	References
CH ₃ Li	250° (dec)	Insol.	d 0.769 gm/cm ³	7
C ₂ H ₅ Li	95°	Sol.	Vapor press. at 60° C, 4×10^{-3} mm Hg $\Delta H_v = 28$ kcal/mole, d 0.883 gm/cm ³	8, 9, 10a
<i>n</i> -C ₃ H ₇ Li	Liq. at r.t.	Sol.	—	5
<i>i</i> -C ₃ H ₇ Li	52°	Very sol.	—	11
<i>n</i> -C ₄ H ₉ Li	Liq. at -76°	Sol.	Distills at 80-90° C/10 ⁻⁴ mm Hg d ₂₅ 0.765 gm/cm ³	9, 12
<i>sec</i> -C ₄ H ₉ Li	Liq.	Sol.	d ₂₅ 0.783 gm/cm ³	12
<i>tert</i> -C ₄ H ₉ Li	Sublimes at 70°/0.1 mm Hg	Very sol.	—	13
(CH ₃) ₃ SiCH ₂ Li	Sublimes at 100°	Sol.	—	14
CH ₂ =CHLi	Solid, r.t.	Insol.	—	15, 16
CH ₂ =CH—CH ₂ Li	Solid, r.t.	Insol.	—	17
CH ₂ —CH ₂ —CHLi	Solid, r.t.	Insol.	—	18
C ₆ H ₅ Li	Solid	Insol.	Colorless	5, 19

Ziegler and Colonius (6) pioneered the use of alkyl halides in a suitable solvent, e.g.,



On partial removal of solvent from the filtered solution, the solid organolithium compound crystallizes out, and may be purified by subsequent recrystallization. Unfortunately, not very many organolithium compounds possess the desired solubility properties in hydrocarbon solvent and a melting point above room temperature. The physical properties of a number of compounds are given in Table I (5, 7-19). It is interesting that the *n*-alkyl compounds above *n*-propyl are liquids. It appears that increased branching at the lithium-bearing carbon leads to higher melting points, since isopropyllithium and *tert*-butyllithium are solids, at room temperature. A number of compounds previously unavailable as pure solids have been prepared recently by Seyferth and co-workers using transmetallation reactions (15*a,b*, 17, 18, 20).

The organolithium compounds interact strongly with basic solvents such as ethers or amines. It is generally not possible, therefore, to prepare solvent-free samples from preparations carried out in such solvents. Methyllithium constitutes an exception; most of the ether can be driven off from methyllithium etherate without appreciable decomposition of the remaining compound (21). This preparation, though not desirable, is made necessary by the failure of the usual methods. It should be noted that preparations of CH_3Li by a halogen-metal interchange using ethyllithium and methyl iodide or dimethyl mercury (22) (this method derives its driving force from the insolubility of CH_3Li in hydrocarbons) are not satisfactory. A 1:1 complex of the formula $\text{C}_2\text{H}_5\text{Li}:\text{CH}_3\text{Li}$ rather than pure methyllithium precipitates from the solution (23, 24). Complex formation can be avoided by using *n*-butyllithium rather than ethyllithium, but some LiI appears in the product. A similar complex formation has been noted in the preparation of cyclopropyllithium via the transmetallation reaction between tetra-cyclopropyltin and *n*-butyllithium in pentane (18).

II

STRUCTURES OF SIMPLE ORGANOLITHIUM COMPOUNDS

A. X-Ray Crystal Structure Determinations

The X-ray structural work reported to date on alkylolithium compounds has been very important in substantiating the structural scheme proposed

on the basis of less definitive spectral data, and in providing accurate geometrical data for use in other work. The first important X-ray work was reported by Dietrich (8) who obtained a three-dimensional Fourier projection of ethyllithium from single-crystal data. Portions of the unit cell are depicted in Figs. 1 and 2; some of the relevant bond distances and angles

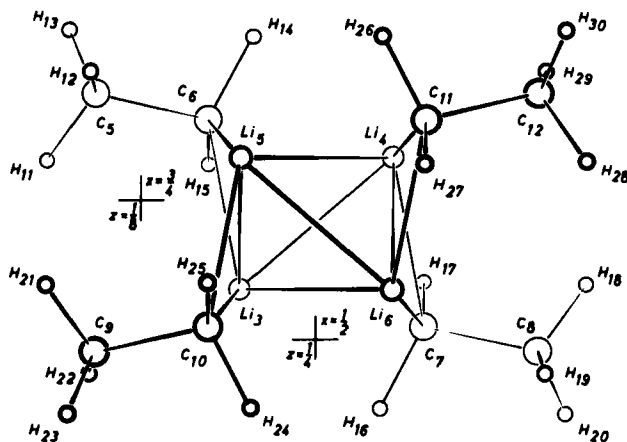


FIG. 1. Portion of the unit cell in ethyllithium (8).

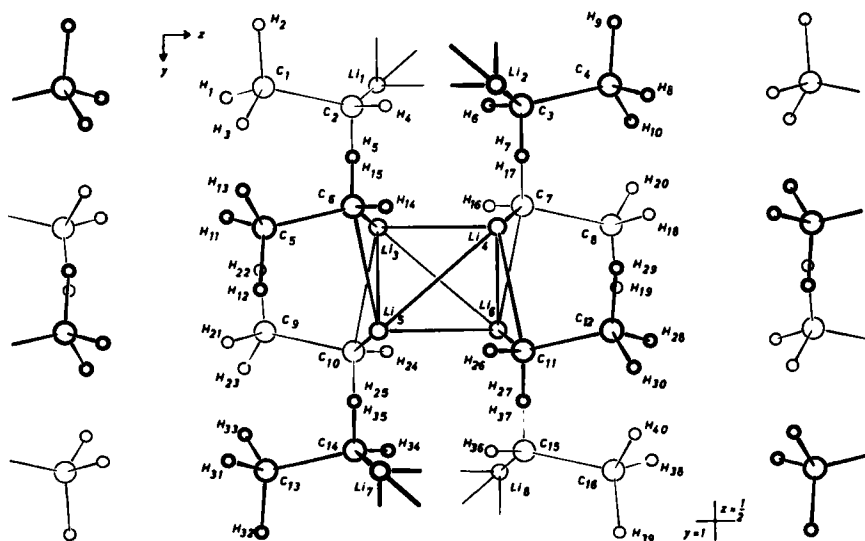


FIG. 2. Portion of the unit cell in ethyllithium (8).

are listed in Table II. The structure of methyllithium has been deduced by Weiss and Lucken (7) on the basis of powder diffraction data (methyllithium

TABLE II
BOND ANGLES AND BOND DISTANCES IN
SOLID ETHYLLITHIUM^{a, b}

Li ₃ —Li ₅	2.424 ± 0.009
Li ₃ —Li ₄	2.603 ± 0.010
Li ₃ —Li ₆	2.633 ± 0.008
Li ₃ —C ₁₀	2.188 ± 0.004
Li ₅ —C ₁₀	2.252 ± 0.006
Li ₆ —C ₁₀	2.468 ± 0.005
Li ₇ —C ₁₀	2.531 ± 0.004
Li ₅ —C ₈ —Li ₃	66.1 ± 0.2°
Li ₄ —C ₈ —Li ₃	66.7 ± 0.2°
Li ₄ —Li ₃ —Li ₅	63.1 ± 0.2°

^a Reference (8). Bond distances given in Å.

^b Refer to Figs. 1 and 2 for numbering.

has so far not been obtained in other than microcrystalline form despite numerous attempts at growing single crystals). The unit cell is cubic, with both carbon and lithium on special positions, so that the number of parameters is sufficiently small to permit fixing both carbon and lithium locations. The hydrogen positions are, however, not known. The methyllithium structure is depicted in Fig. 3; relevant bond distances and angles are given in Table III.

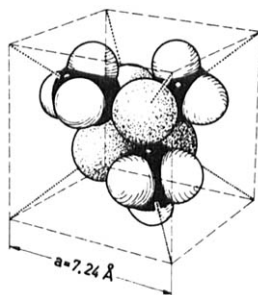


FIG. 3. Structure of methyllithium (7).

TABLE III
BOND DISTANCES AND BOND ANGLES IN
SOLID METHYLLITHIUM^a

Li—Li	$2.56 \pm 0.12 \text{ \AA}$
Li—C	$2.28 \pm 0.06 \text{ \AA}$
Li—C'	$2.52^b \pm 0.12 \text{ \AA}$
C—C	$3.69 \pm 0.10 \text{ \AA}$
Li—C—Li	$68.3^\circ \pm 0.2^\circ$

^a Reference (7).

^b Distance from a lithium atom to the nearest carbon of an adjacent tetramer.

Although the unit cells are quite different in these two structures, it is clear that a tetrameric grouping forms the distinguishable structural unit. This is unambiguously the case with methyllithium; in ethyllithium there is some distortion of the tetramers, probably as a result of the lower symmetry of the ethyl group. In both structures there is also very clearly some interaction between tetramer units. In ethyllithium the interaction is two-dimensional in character, and the tetramers are distorted accordingly. In methyllithium the high symmetry and low steric requirement of the methyl group permit three-dimensional association of the tetramer units so that the site symmetry of the tetramers remains high, and no distortion results.

The principal points of interest in the structural details are the short lithium–lithium distances in the tetramers (2.56 \AA vs. 2.67 \AA in Li_2), and C—Li distances somewhat longer than the sum of C (sp^3) and Li single bond radii. There is a further point that the C—Li—C bond angles are sharp, a characteristic of bond angles in electron-deficient bridging (2). Other aspects of the X-ray structural data will be referred to in later discussion.

B. Mass Spectra

The mass spectrum of ethyllithium vapor (25) reveals the presence of a number of ionic species (Table IV). On the basis of their low appearance potentials, Li_6R_5^+ and Li_4R_3^+ are adjudged to be the only parent species in the vapor; the others result from these two by subsequent fragmentation. Double oven experiments demonstrate that separate precursors of both Li_6R_5^+ and Li_4R_3^+ are indeed present and in equilibrium in the effusion

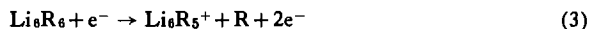
TABLE IV
MASS SPECTRUM OF ETHYLLITHIUM VAPOR^{a, b}

Mass number	Ion	Relative intensity	Appearance potential (ev)
187	Li ₆ R ₅ ⁺	24	7.7 ± 0.5
151	Li ₅ R ₄ ⁺	1.3	12.5 ± 0.5
115	Li ₄ R ₃ ⁺	47.5	8.0 ± 0.5
79	Li ₃ R ₂ ⁺	15	11.7 ± 0.5
43	Li ₂ R ⁺	100	11.7 ± 0.5
7	Li ⁺	14	14 ± 2

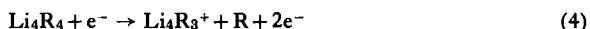
^a Reference (25).

^b Electron energy, 75 ev.

cell. The ionization processes which follow upon electron impact are presumably



and



Neither of the parent molecular ions was detected. As a matter of interest it might be noted that use of lithium metal of varying Li⁶/Li⁷ ratio is very useful in establishing unambiguously the number of lithium atoms in any particular ionic species.

The appearance potential data is valuable as an indication of the ease with which an alkyl radical is lost following ionizing electron impact, and in showing that the lithium atoms are very tightly bound in the parent species. On the basis of these results it is necessary to think in terms of structures with special geometrical requirements (only hexamer and tetramer), involving an inner core of lithium atoms, and less tightly bound alkyl groups. The oven temperature was estimated to be about 87° C; the total vapor pressure of ethyllithium in the effusion cell was estimated to be on the order of 0.1 mm, in reasonable agreement with an extrapolated value based on Chaikin's data (10a). The absence of any lower weight species such as monomer or dimer under these conditions is remarkable, and argues for very stable polymeric species.

C. Colligative Properties in Hydrocarbon Solution

Association of organolithium compounds in hydrocarbon solution has been extensively investigated. Many of the reported data are of little value, however, because proper precautions regarding impurities were not taken.

The boiling point elevation experiment with compounds as reactive as the organolithium compounds is particularly susceptible to effects of traces of oxygen, water, or other impurities. The freezing point lowering experiment avoids this difficulty to some extent, but is limited insofar as choice of

TABLE V
COLLIGATIVE PROPERTY DATA FOR HYDROCARBON SOLUTIONS
OF ALKYL LITHIUM COMPOUNDS

Compound	Solvent	Conc. range (molality in monomer)	n	Method ^a	References
C ₂ H ₅ Li	C ₆ H ₆	0.02–0.23	6.07 ± 0.35	F	23
	C ₆ H ₁₂	0.02–0.10	5.95 ± 0.3	F	26a,b
<i>n</i> -C ₄ H ₉ Li	C ₆ H ₆	0.5–3.4	6.25 ± 0.06 ^b	I	27
	C ₆ H ₁₂	0.4–3.3	6.17 ± 0.12 ^b	I	27
(CH ₃) ₃ CLi	C ₆ H ₆	0.05–0.18	3.8 ± 0.2	B	13
	C ₆ H ₁₄	0.05–0.23	4.0 ± 0.2	B	13
(CH ₃) ₃ SiCH ₂ Li	C ₆ H ₆	0.6–2.78	4.0 ± 0.2	B	28
	MP ^c	0.2–1.2	3.9 ± 0.2	B	28
	C ₆ H ₆	0.06–0.49	4.0 ± 0.11	F	29

^a I, isopiestic; F, freezing point lowering; B, boiling point elevation.

^b The authors ascribe the deviation from 6.0 to slight decomposition, with formation of butylene.

^c Methyl pentane.

solvent is concerned. Isopiestic methods have been employed, but difficulties arise from the length of time required to reach equilibrium. Table V (13, 23, 26a–29) summarizes the more recent and—in the writer's view—more reliable colligative property data for a number of organolithium compounds. The solvents represented are the hydrocarbons only; solutions in basic solvents are dealt with in Section III.

The data of Table V seem to establish that the alkyl lithium compounds exist in hydrocarbon solution as either hexamer or tetramer. There is no evidence in any of the data for dissociation of these species in the lower

concentration range. The more highly branched alkyl groups appear to lead to tetramer, probably because the alkyl groups are less crowded than in the hexamer. There is evidence that increasing chain length results in a lower degree of association. Thus, *n*-dodecyl lithium is reported to be approximately tetrameric in benzene (30). Further, Morton and co-workers have concluded that long-chain species of the form R—CHR'Li, where R is a polystyryl or polyisoprenyl group, formed in alkyllithium-initiated polymerization reactions, are dimeric (31).

D. Infrared Spectra

The infrared spectra of organolithium compounds in solid, vapor, and solution phases have been reported. Because the compounds are subject to thermal decomposition and are in general not very volatile, the reported vapor-phase spectra are probably not as reliable as the solution data.

None of the absorptions appearing above 650 cm^{-1} in any organolithium spectra shows a detectable mass effect upon substitution of Li^6 for Li^7 (13, 32, 33). It follows that the carbon–lithium valence vibrations lie in the longer wavelength region. For the compounds in hydrocarbon solution, or in the solid or vapor state, the normal modes involving lithium–carbon motion must be complex, involving the skeletal modes of the polymeric framework. The highest frequency modes, e.g., the totally symmetric Raman-active mode of the *tert*-butyllithium tetramer in benzene solution (13), consist largely of carbon–lithium stretch.

The data reported for a number of organolithium compounds in various states are given in Tables VI (13, 30, 32, 33, 34) and VII. The mass effect observed upon substitution of Li^6 for Li^7 is of particular interest, in that its magnitude is a rough measure of the extent to which lithium motion is involved in the normal mode. If only lithium motion were involved, the ratio of frequencies would be $\nu_{\text{Li}^6}/\nu_{\text{Li}^7} = (7/6)^{1/2}$, or 1.08. It is of interest that this ratio is observed for the aforementioned symmetric mode of the *tert*-butyllithium tetramer. This vibration can therefore be visualized as a symmetric motion of the lithium atoms along the local threefold axes of the tetramer.²

The effect of a basic solvent upon the low-frequency modes is discernible in only the highest frequency mode, because solvent absorption obscures the lower frequency region. The $550\text{--}500\text{ cm}^{-1}$ band is shifted to lower

² There is, of course, the possibility that one of the frequencies in this comparison is shifted by a Fermi resonance.

frequency, but the fact that it persists is indication that the organolithium compounds remain associated to some degree in basic solvents. There is slight evidence also that the isotopic mass effect is lower in basic solvent.

TABLE VI
INFRARED SPECTRA OF ORGANOLITHIUM COMPOUNDS
IN THE 600–300 cm^{-1} REGION

Compound	Physical state	ν_{Li}^7	ν_{Li}^8	$\nu_{\text{Li}}^8/\nu_{\text{Li}}^7$	References
$\text{C}_2\text{H}_5\text{Li}$	Vapor	531	550	1.036	30
		566	570 (?)	1.006	32
	Mull	535	565	1.056	32
		465	496	1.066	
		340	362	1.065	
		565	—	—	34
	Benzene	445	—	—	
		318	—	—	
		530	—	—	34
		376	—	—	
$\text{C}_6\text{H}_5\text{Li}$	Hexane	532	550	1.034	33
	Benzene	527	550	1.044	30
	<i>n</i> -Butyl ether	516	530	1.027	30
	Mull	421	429	1.019	32
		378	390	1.032	
$(\text{CH}_3)_3\text{CLi}$	Benzene	521 (R)	563 (R)	1.081	13
		480	496	1.033	
		420	429	1.021	

TABLE VII
EFFECT OF SOLVENT AND ISOTOPIC SUBSTITUTION UPON THE INFRARED
ABSORPTIONS OF ETHYLLITHIUM^a

	C_6H_{14}	C_6H_6	$(\text{C}_2\text{H}_5)_2\text{O}$	$(n\text{-Bu})_2\text{O}$
$\text{CH}_3\text{CH}_2\text{Li}^7$	528	527	497	516
$\text{CH}_3\text{CH}_2\text{Li}^8$	550	550	—	530
$\text{CD}_3\text{CH}_2\text{Li}^7$	529	—	504	512
$\text{CH}_3\text{CD}_2\text{Li}^7$	514	512	479	—
$\text{CD}_3\text{CD}_2\text{Li}^7$	515	513	481	—

^a Reference (30).

E. Dipole Moments

A number of dielectric constant studies of organolithium compounds have been reported and interpreted without cognizance of the hexameric character of the lower molecular weight *n*-alkyllithium compounds. Table VIII (35, 36, 37) lists the results of a number of dielectric constant studies; the

TABLE VIII
DIPOLE MOMENT RESULTS FOR *n*-ALKYLLITHIUM COMPOUNDS IN HYDROCARBON
SOLUTION AT 25° C

Compound	Solvent	μ (Debye)	P_A Correction	References
(C ₂ H ₅ Li) ₆	C ₆ H ₆	1.5	44 cm ³	35
(C ₂ H ₅ Li) ₆	C ₆ H ₆	1.73	None	36
(C ₂ H ₅ Li) ₆ ^a	C ₆ H ₁₄	2.5	None	37
(C ₄ H ₉ Li) ₆	C ₆ H ₆	1.43	50 cm ³	35
(C ₄ H ₉ Li) ₆ ^a	C ₆ H ₁₄	2.6	None	37
(C ₅ H ₁₁ Li) ₆ ^a	C ₆ H ₁₄	2.6	None	37
(C ₁₂ H ₂₅ Li) ₆ ^{a, b}	C ₆ H ₁₄	2.4	None	37

^a Dipole moments calculated from data reported in the reference; the original authors assumed monomeric association.

^b If this compound is in fact tetrameric in solution (Section II, C), multiply dipole moment value by 0.81.

molecularity of the organolithium compound assumed in the calculation is as shown. An accurate determination of the molecular dipole moment of the hexameric species is not possible from hydrocarbon solution studies because the magnitude of the atomic polarization is unknown. The fact that rather high intensity absorptions are seen in the infrared in the 550–300 cm⁻¹ range portends that high-intensity absorptions arising from the skeletal deformation modes may occur at longer wavelengths, and thus that the atom polarization may be high. Rogers and Brown attempted to estimate this factor in calculating the dipole moments of the ethyllithium and *n*-butyllithium hexamers in benzene (35). From the best evidence available, the moments of these two species are not zero, even though the proposed geometry for the hexameric skeleton (Section II, F) would preclude a moment arising in the framework bonding itself. The effect has been ascribed to a noncancellation of alkyl group moments owing to internal rotations (38).

F. Electronic Structure

The simplest view of the electronic structures of the tetrameric and hexameric alkyllithium species is one in which the bonding is considered in terms of localized multicenter bonding sites (13, 38). The structure of the tetramer will be discussed in detail, since the experimental data is most complete for this species. It is evident from inspection of Figs. 1, 2, and 3 that each lithium atom is associated with three alkyl carbon atoms. Assuming

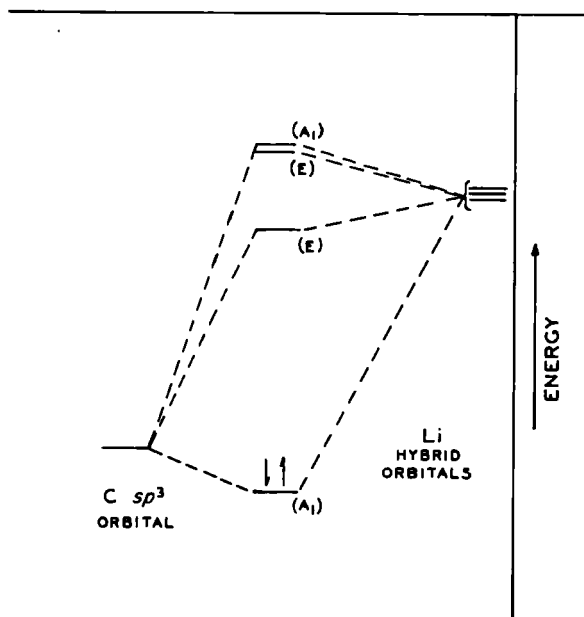


FIG. 4. Energy level diagram for a localized four-center molecular orbital. The symmetry symbols refer to the pseudo- C_{3v} symmetry of the localized MO.

that the lithium atom employs three valence shell orbitals in the bonding, a set of three (approximately) sp^2 hybrid orbitals, directed toward the alkyl carbon atoms, may be visualized. Three such lithium atomic orbitals and a single carbon sp^3 (approximately) orbital overlap to produce a four-center localized molecular orbital. One electron pair is accommodated in the lowest energy of these. The energetics of this bonding situation are shown diagrammatically in Fig. 4. Certain characteristics of electron-deficient bridge bonding are easily identified in the tetramer structure. The C—Li distance is longer than expected for a single carbon–lithium bond; in the tetramer structure, each carbon–lithium bond is formally a one-third bond.

Metal-metal distances are characteristically short, as seen also in $\text{Al}_2(\text{CH}_3)_6$, or $[\text{Be}(\text{CH}_3)_2]_n$. The Li—C—Li angle is sharp (68° in CH_3Li), a characteristic also seen in the two structures just alluded to.

The structure of the hexamer species remains conjectural to some extent, since a hexameric species has not yet been observed in X-ray work. The hexamer and tetramer species must, however, be closely similar in energy; the vapor of ethyllithium contains both species, hydrocarbon solutions contain predominantly hexamers, and the solid state consists of loosely associated tetramers. Further, the infrared spectra of ethyllithium in the solid state and in hydrocarbon solution are closely similar. A model for the hexamer which involves the same bonding formalism just presented for the

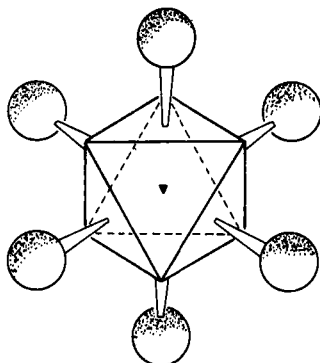


FIG. 5. Model of the alkyl lithium hexamer structure.

tetramer can be formed (23, 38) by locating the lithium atoms at the apices of an octahedron. This figure possesses eight trigonal faces; alkyl carbon atoms are placed on three of the top four faces, forming in each case a four-center localized molecular orbital as described above. The other three alkyl groups are then placed on the opposing three faces of the lower half of the octahedron. Some distortion from an octahedral arrangement of the lithium atoms presumably occurs, but such a structure, possessing D_{3d} symmetry (Fig. 5), provides a satisfactory working model for the hexamer. Polymeric species other than tetramer and hexamer which embody the four-center bonding arrangement are not likely to occur, since they would require severe distortion of the immediate environment about the lithium atoms, or undue crowding of the alkyl groups. For example, an octamer in which the lithium atoms are arranged at the apices of an Archimedes antiprism, and the alkyl groups are on the eight trigonal faces, is possible, but would be subject to the shortcomings just mentioned. It is significant

that no evidence was found in the mass spectrum of ethyllithium (25) for a species with molecular weight greater than the hexamer.

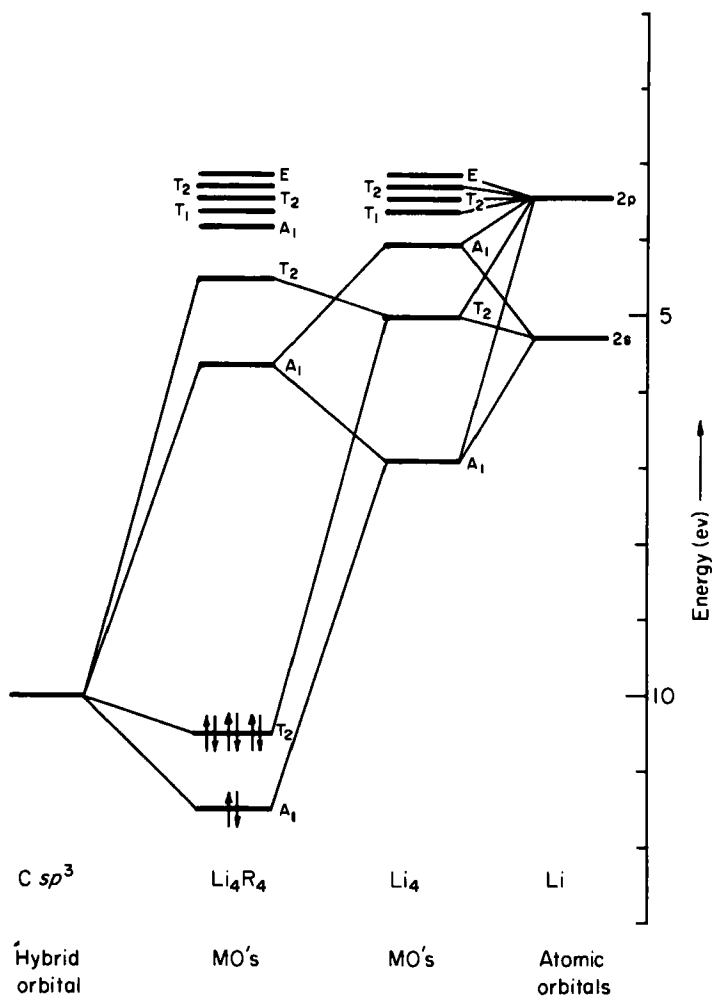
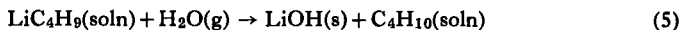


FIG. 6. Energy level diagram for alkyl lithium tetramer (7).

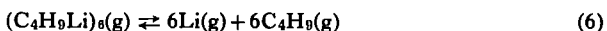
An alternative, more general view of the bonding in the tetramer has been proffered by Weiss and Lucken (7). The energy level diagram which they propose is shown in Fig. 6. The shortness of the Li—Li distances suggests that the metal $2s$ and $2p$ orbitals may be combined in accordance with symmetry requirements to form a set of core molecular orbitals. The

carbon atomic orbitals, of approximately sp^3 hybridization, interact with the core orbitals to form molecular orbitals which are effectively delocalized over all participating atoms. Although the energies given for the molecular orbitals in Fig. 6 must be regarded as only rough estimates, the general picture of the bonding situation is probably close to correct. Of particular interest is the large separation of about 5 eV between the occupied T_2 level and the lowest vacant (A_1) level. The absence of absorptions arising from electronic transitions in alkyllithium compounds (39) is in agreement with this result. (The absence of absorptions may also be due, however, to a low transition moment for the lowest energy singlet transition.) The energy of the lowest vacant orbital compares with that found in aromatic compounds which act as acceptors in charge-transfer complex formation (40). The possibility that the electron-deficient polymeric alkyllithium compounds might act as charge-transfer acceptors toward suitable bases of the π type is actively under investigation.

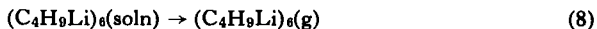
Fowell and Mortimer (41) have measured the heat of the reaction



from which they derive a value of -31.4 ± 0.7 kcal/mole for the heat of formation of *n*-butyllithium in solution. There are two reactions for which it is desirable to have estimates of the enthalpy changes



A value for the enthalpy of reaction (7) in solution would be of perhaps greater utility than a gas-phase value. In order to estimate ΔH for Eq. (6), the heat of formation of *n*-butyllithium hexamer in the gas phase must be estimated. Fowell and Mortimer have estimated the heat of dissociation of the C—Li bond without taking into account the hexameric character of alkyllithium compounds either in solution or in the gas phase. An estimate of ΔH for the process



can be made by ignoring the heat of solution of alkyllithium compounds in hydrocarbon solution, which is undoubtedly small, and by estimating a heat of vaporization from the data provided by Chaikin (10a). Fowell and Mortimer mention an estimated heat of vaporization of *n*-butyllithium liquid of 33 kcal/mole. Chaikin's values of 27.9 kcal/mole for ethyllithium and 25.6 for *n*-butyllithium apply to a good approximation regardless of the

molecularity assumed for the vapor species. The important point, however, is not which particular value is chosen for ΔH_v , but the recognition that *it applies to the hexameric species*. The heat of formation of gaseous *n*-butyllithium hexamer is then estimated as $6 \times (-31.4) + 26 = -162$ kcal/mole. The heat of reaction (6) is then $(6 \times 37.07) + (6 \times 18.5) + 162 = +495$ kcal/mole. This corresponds to an average stabilizing energy of 82 kcal/mole per bonding electron pair in the framework orbitals, if it is assumed that changes in bond energies of the alkyl group in reaction (6) are negligible. This means that the average of the framework bonding electron pair energies lies $82/23 = 3.56$ eV below the average of the lithium 2s and alkyl $2sp^3$ energies. If the same value is assumed to apply to the methyl-lithium tetramer, it follows that the A_1 and T_2 energies are at $-11.3 + 3\beta$ eV and $-11.3 - \beta$ eV for the A_1 and T_2 levels, respectively (Fig. 6). Assuming $\beta = -0.3$ eV, this gives -12.2 and -11.0 eV, respectively, for the A_1 and T_2 levels. This is somewhat greater stability than indicated by Weiss and Lucken but the general agreement is good. It would be of great value to have the appropriate calorimetric and other thermodynamic data for an organolithium compound which is associated as tetramer, e.g., $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$.

The enthalpy change in reaction (7) is unfortunately not known for any organolithium compound.

G. Nuclear Magnetic Resonance Spectra

Both H^1 and Li^7 magnetic resonance spectra have been observed for organolithium compounds, in a variety of solvents. The most important result of NMR studies, insofar as structural information is concerned, is to provide insights into exchange processes which may subsist in the solutions.

The chemical shifts of protons attached to the lithium-bearing carbon in alkyllithium compounds are found at high fields, as expected. A few representative chemical shift values are listed in Table IX (13, 14, 18, 23, 43, 44). Spin-spin couplings involving the protons have been utilized in assigning the isomers in vinylic systems (44).

Exchange processes for an organolithium compound in solution might be either intra- or intermolecular. An intramolecular exchange of alkyl groups among the bonding sites in the polymer should have a fairly low activation energy (38); to date no evidence regarding this type of exchange is available. An intermolecular exchange might proceed either through dissociation of an alkyllithium polymer into less-associated fragments (e.g., dissociation of a hexamer into tetramer and dimer), or through a bimolecular interaction of

TABLE IX
SELECTED CHEMICAL SHIFT VALUES FOR PROTONS IN ORGANOLITHIUM
COMPOUNDS

Compound	Solvent	Chemical shift τ	References
CH_3Li	Ether	11.94	23
$\text{CH}_3\text{CH}_2\text{Li}$	Ether	11.10	23
	Benzene	10.83	38
$(\text{CH}_3\text{CH}_2)_4\text{AlLi}$	Ether	10.44	42
$(\text{CH}_3)_3\text{CLi}$	Benzene	9.01	13
$(\text{CH}_3)_3\text{SiCH}_2\text{Li}$	Benzene	11.96	14
$\text{CH}_2\text{CH}_2\text{CHLi}$	THF	12.5	18, 43
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHLi}$	Ether	3.70	44
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHLi}$	Ether	3.30	44

two polymeric units. In basic solvents, in which the compounds may be present as solvated, less-associated species, a heterolytic cleavage of the form



is possible as well.

It has been reported that a mixture of ethyllithium and *tert*-butyllithium in benzene exhibits more than one Li^7 resonance (45). The existence of distinguishable Li^7 resonances for both ethyllithium and *tert*-butyllithium in benzene has been noted for temperatures up to 45°C (46). These data, which require that intermolecular exchange of *tert*-butyl and ethyl groups proceeds with an exchange time τ_e of about 0.01 sec or longer, indicate a considerable stability for the polymeric framework in hydrocarbon solvent. It has been shown also that intermolecular alkyl group exchange in ethyllithium in toluene is slow (47) (i.e., that the exchange time, τ_e , is on the order of 0.1 sec or longer) at room temperature.

The limited amount of work which has been reported so far for alkyl-lithium compounds in basic solvents indicates that intermolecular exchanges proceed much more easily than in hydrocarbon solvents (47, 48a). The use of NMR in the careful study of kinetic parameters of exchanges is potentially of great value. A recent study of the Li^7 resonances in ether reveals that the simple alkyl compounds are tetrameric in ether at temperatures of -50°C and lower (48b).

The Li^7 nucleus possesses a spin of 3/2, and a sizable quadrupole moment. Quadrupolar relaxation of the Li^7 resonance in toluene solutions of $\text{Li}^7\text{C}_2\text{D}_5$

and $\text{Li}^{7}\text{C}(\text{CH}_3)_3$ may therefore determine the NMR linewidths. A study of the temperature dependences of the Li^{7} linewidths in these two cases provides rough estimates of the quadrupole coupling constants, 0.57 mc/sec and 0.14 mc/sec for ethyllithium and *tert*-butyllithium, respectively. The interesting possibility exists that the lower value of quadrupole coupling constant is associated with the tetramer configuration, and the higher with hexamer, but further examples are required to test this. In a study of a related pair of compounds, lithium *n*-butoxide and lithium *tert*-butoxide, the Li^{7} linewidth was found to be much wider in the *n*-alkyl compound, both in solution and in the solid state (49). This difference is very likely due to a difference in the geometry of the prevalent polymeric species, rather than to any difference in the ionicity of the $\text{Li}-\text{OR}$ bond with variation in the alkyl group.

III

ACID-BASE BEHAVIOR

An understanding of the acid-base properties of organolithium compounds is essential to an understanding of the mechanisms by which they undergo chemical reaction. It is necessary to begin with a definition of what is meant by the terms acid and base in the present context. The organolithium hexamer and tetramer species described above are Lewis acids, a property which they share with related organometallic compounds such as trialkylaluminum compounds (50). The polymers may exhibit acid character by forming an addition compound with *n*-type bases (51) such as amines or ethers. An interaction of this type between ethyllithium hexamer and triethylamine or lithium ethoxide in hydrocarbon solvent, without dissociation of the hexamer, has been demonstrated (23, 52). The interaction is presumed to occur via coordination of base to one of the two vacant faces of the hexamer molecule (Fig. 5). A second base molecule may coordinate on the opposite vacant face of the hexamer, to form an $(\text{RLi})_6\text{B}_2$ species. If the base is a strong donor, the hexameric species may dissociate in the presence of excess base, as does ethyllithium in the presence of excess triethylamine in benzene (23). An analogous interaction of base with tetramer in advance of dissociation is not possible, as no vacant faces exist in the tetramer structure. It is significant, therefore, that no evidence could be adduced from dielectric constant studies for an interaction of triethylamine with *tert*-butyllithium (53). The organolithium compounds may also interact

with bases by dissociating. Typical of the adducts formed in this way are $(\text{LiC}_2\text{H}_5)_2 \cdot (\text{NR}_3)_2$ (23) and $(\text{LiC}_4\text{H}_9)_2(\text{OR}_2)$ (54). These species were proposed on the basis of kinetic or colligative property data obtained upon addition of the base to hydrocarbon solutions of the alkyllithium compounds. It is still not entirely clear what molecularity the organolithium compounds possess in the pure basic solvent. On the basis of boiling point elevation experiments phenyllithium and benzylithium appear to be dimeric in ether (19); results obtained from similar experiments for *n*-alkyllithium compounds in ether, while they indicate association (30), cannot be relied upon because the solutes react rather rapidly with ether (55).

A number of solid complexes of various organolithium compounds with various bases have been reported, e.g., $\text{C}_4\text{H}_9\text{Li} \cdot \text{S}(\text{CH}_3)_2$ (56); $[(\text{CH}_3)_3\text{CLi}]_2 \cdot \text{THF}$ (53); 9-fluorenyllithium dietherate, a yellow solid (57); phenyllithium dioxanate, a colorless solid of formula $2\text{C}_6\text{H}_5\text{Li} \cdot 3\text{C}_4\text{H}_8\text{O}_2$ (58). The structures of none of these compounds are known, but they serve as examples to establish that the alkyllithium compounds do behave as Lewis acids toward *n*-type bases.

Solvation of the organolithium polymeric species, with possibly some disruption of the polymers to less-associated species, leads to adducts which may function as a source of carbanions; in this sense the adducts behave as bases in furnishing a nucleophilic moiety. It is important to realize, however, that such basic behavior can occur only in the presence of a basic solvent, or it requires a strong Lewis acid. Examples of the latter situation are found in the reaction of alkyllithium compounds with other organometals, as described in the following section.

IV

COMPLEX ORGANOLITHIUM COMPOUNDS

Both alkyl and aryllithium compounds are capable of reacting with other organometallic compounds to form mixed species of well-defined stoichiometry, which may or may not contain coordinated solvent. The earliest work of this kind carried out in a systematic manner is that of Hein and collaborators in the 1920's (59). Ethyllithium was found to dissolve in triethylaluminum and diethylzinc. In the former instance a fairly high electrical conductance, presumably due to the compound $\text{LiAl}(\text{C}_2\text{H}_5)_4$, was observed. Many examples of solid mixed organometallic complexes are reported in the literature (60), e.g., $\text{Li}_2\text{Zn}(\text{CH}_3)_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ (61). Wittig and co-workers

have been active in studying such species among the aryl derivatives (62), e.g., $\text{LiMg}(\text{C}_6\text{H}_5)_3$, $\text{LiB}(\text{C}_6\text{H}_5)_3$, and $\text{LiSb}(\text{C}_6\text{H}_5)_6$.

There is a dearth of structural information about the mixed organometallic compounds. Lithium aluminum tetraethyl is isostructural with dimethylberyllium (42), as one might expect after noting that the ratio of metal atoms to alkyl groups is the same in the two compounds. The structure of $\text{LiAl}(\text{C}_2\text{H}_5)_4$ is shown in Fig. 7; the relevant bond distances and angles are

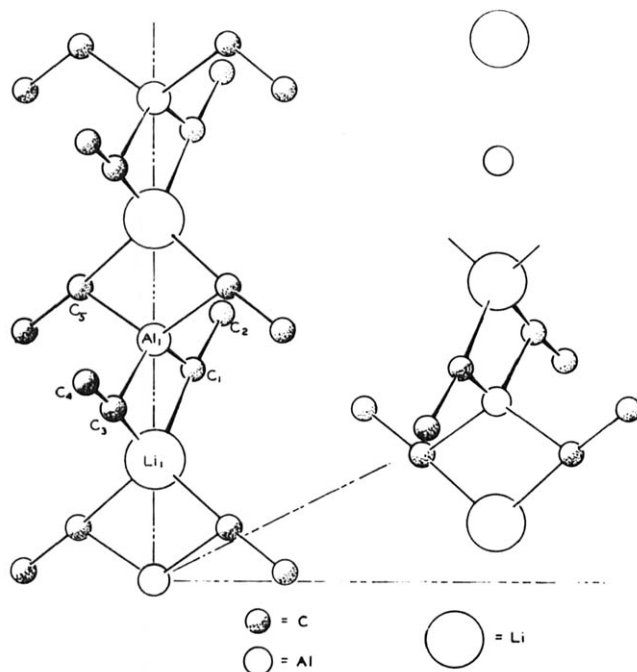


FIG. 7. Structure of lithium aluminum tetraethyl (42).

given in Table X. Insofar as covalency can be ascribed to the structure, the alkyl group carbon atom forms a three-center bridge bond between lithium and aluminum. The metal-carbon bridge bonding is unsymmetrical, and indeed the structure is not far removed from ionic, with alternating lithium cations and $\text{Al}(\text{C}_2\text{H}_5)_4^-$ anions in a linear array. Such covalency as does exist in the chain arises from an overlap of lithium orbitals directed along the chain axis, with orbitals of the $\text{Al}(\text{C}_2\text{H}_5)_4$ group, as shown schematically in Fig. 8. Since covalent bonding involving lithium is slight, lithium $2p$ orbitals are probably involved to only a slight extent.

TABLE X
BOND ANGLES AND BOND DISTANCES IN LITHIUM ALUMINUM TETRAETHYL^{a, b}

Bond distance (Å)		Bond angle	
Al ₁ —C ₁	2.023 ± 0.006	C ₃ —Al ₁ —C ₁	112.1° ± 0.6°
Al ₁ —Li ₁	2.706	C ₃ —Al ₁ —C ₅	108.2° ± 0.3°
Al ₁ —Li ₂ ^c	7.061	Al ₁ —C ₁ —C ₂	109.2° ± 0.5°
C ₁ —C ₂	1.523 ± 0.012	Al ₁ —C ₁ —Li ₁	77.2° ± 0.3°
C ₁ —C ₃	3.360 ± 0.011	C ₁ —Li ₁ —C ₃	93.6° ± 0.3°
Li ₁ —C ₁	2.302		

^a Reference (42).

^b See Fig. 7 for identification of numbered atoms.

^c This is the distance between chains, normal to the chain axes.

There is no structural information available for the analogous LiBR₄ systems; the BR₄[−] system is probably not very stable because of the small size of the boron atom. Delocalization of charge into lithium orbitals would reduce electron repulsions. One expects on these grounds that LiBR₄ compounds will evince a greater degree of covalent character than the aluminum analogs. It is of interest in this context that LiB(CH₃)₃(C₂H₅) is remarkably soluble in benzene (63).

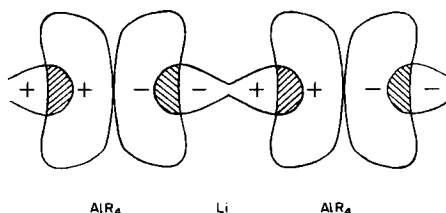


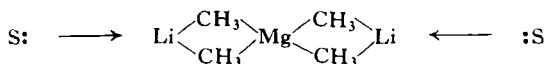
FIG. 8. Schematic illustration of covalent bonding in solid LiAlR₄ and related compounds.

Mixed organometallic compounds can be expected to possess different structures in solution or in the vapor phase than in the solid state. The stoichiometries observed for solid adducts recovered from solutions may not correspond to the stoichiometries of the stable species present—if indeed mixed compound formation persists at all—in solution. It has been argued on chemical evidence that free organolithium is not present in ethereal solutions of LiBe(C₆H₅)₃ (19), or THF solutions of LiB(C₄H₉)₄

(64). The presence of free ethyllithium in appreciable concentrations in ether solutions of $\text{LiAl}(\text{C}_2\text{H}_5)_4$ is excluded on the basis of the observed Li^7 magnetic resonance spectrum (42). On the other hand, Wittig and co-workers conclude that $\text{LiMg}(\text{C}_6\text{H}_5)_3$ is appreciably dissociated in ether at room temperature (19).

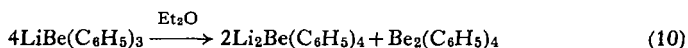
The proton magnetic resonance spectra of solutions of methyllithium and dimethylmagnesium in ether provide demonstration of the nearly complete formation of $\text{Li}_2\text{Mg}(\text{CH}_3)_4$ at lower temperatures (46). The complex does not appear to dissociate appreciably with increasing temperature. Rapid exchange sets in to obliterate the separate resonance lines at temperatures above about -10°C , but extrapolation to higher temperatures indicates that dissociation of the complex is slight at room temperature. It is of particular interest to note that a solid complex of the stoichiometry found in solution has not been isolated.

The structure of the solution complex is probably



where S represents coordinated solvent.

A molecular weight of 320 has been reported from ebulliometric measurements on $\text{LiBe}(\text{C}_6\text{H}_5)_3$ (formula weight 247) in ether over a wide concentration range (19). Possibly the following disproportionation reaction occurs on dissolving of the complex in ether:



If this reaction were to proceed essentially to completion, the apparent molecular weight would be 329.

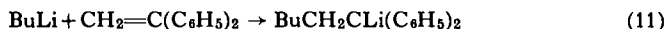
V

KINETICS AND MECHANISMS OF ORGANOLITHIUM REACTIONS

Armed with the structural data and interpretations of the foregoing sections, we may now inquire about the mechanisms by which organolithium compounds undergo chemical reaction.

A. Hydrocarbon Solutions

The alkyllithium compounds are associated in hydrocarbon solvent; the *n*-alkyl compounds, through *n*-butyllithium at least, are hexameric. Since nearly all existing kinetic evidence relates to *n*-butyllithium or ethyllithium, we will confine our considerations to systems involving hexamers. West and Glaze have measured a lithium kinetic isotope effect in the reaction of ethyllithium with benzyl chloride in benzene (65), and report that the reaction is first order in each reactant, with an enthalpy of activation of 17.8 kcal/mole. A distinct Li^6/Li^7 isotope effect was observed. It can be concluded from this that the carbon-lithium bonding is significantly weaker in the transition state than in the ground state. Eastham and Gibson report that the reaction of *n*-butyllithium and 1-bromooctane in hexane is first order in both reactants (54). Ziegler and co-workers (66) concluded that the reaction between ethyl-, *n*-propyl-, *n*-butyllithium and 1,1-diphenylethylene in hydrocarbon solution is first order in each reagent. Evans and George, on the other hand, have studied this system at lower concentrations of alkyllithium reagent and report a one-sixth order rate dependence for the organometallic reagent (67), based on the method of initial rates. This particular reaction is of extraordinary interest in that the reaction product is a new organolithium compound

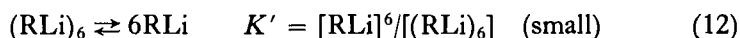


Further addition of olefin to the product is impeded by steric factors. Equation (11) represents the initiation step of an anionic polymerization of an olefin (68); the rate of chain propagation in this case is very slow. It is important that the kinetics of Eq. (11) be thoroughly established, since it does form a prototype system for initiation of anionic polymerization. Preliminary work in the writer's laboratory (69) with ethyllithium concentrations of about 0.1 *M* and 1,1-diphenylethylene concentrations of about 0.05 *M*, employing infrared spectroscopy to follow the disappearance of 1,1-diphenylethylene, have yielded second-order rate plots. The apparent order in alkyllithium, based on the method of initial rates, is in the range 0.7 to 0.95. The experimental details given by Evans and George indicate that meticulous care was taken in their work. It is possible, however, that the spectrophotometric method employed in following the reaction involves some hidden source of error, or that the difference in the experimental results is due to concentration differences. In any case, further work on this important system is desirable.

The initiation of polymerization of styrene by alkyllithium compounds in hydrocarbon solvent has been extensively studied (68, 70, 71). Initiation and chain propagation steps proceed at comparable rates, and the kinetics are quite complex. The initiation reaction is reported to be one-sixth order in alkyllithium, first order in styrene. Since the concentrations of alkyllithium compound employed are very low relative to the concentration of olefin, the method of initial rates is employed in determining reaction order in alkyllithium.

We begin a general consideration of the kinetic results by presenting a few of the more likely pathways by which a hexameric organolithium compound might react with a substrate N. (Subscript 0 indicates initial concentration.)

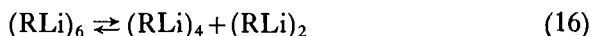
Reaction scheme (i):



$$\text{rate} = k[\text{N}][\text{RLi}] = kK'[\text{RLi}]_0^{1/6}[\text{N}] \quad (14)$$

$$= k_{\text{app}}[\text{N}][\text{RLi}]_0^{1/6} \quad (15)$$

Reaction scheme (ii):



$$K' = [\text{RLi}]_2[(\text{RLi})_4]/[(\text{RLi})_6] \quad (\text{small}) \quad (17)$$



$$\text{rate} = k[(\text{RLi})_2][\text{N}] \quad (19)$$

$$= kK'[(\text{RLi})_6]^{1/2}[\text{N}] = k_{\text{app}}[\text{RLi}]_0^{1/2}[\text{N}] \quad (20)$$

Reaction scheme (iii):



$$K_C = \frac{[(\text{RLi})_6 \cdot \text{N}]}{[\text{N}][(\text{RLi})_6]} = \frac{[\text{C}]}{[\text{N}_0 - \text{C}][\text{H}_0 - \text{C}]} \quad (22)$$

$$[\text{C}] \approx \frac{K[\text{N}_0][\text{H}_0]}{1 + K[\text{H}_0 + \text{N}_0]} \quad (23)$$

if K is small, $[\text{C}] \approx K[\text{N}_0][\text{H}_0]$

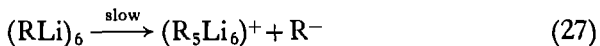
$$\text{rate} = k[\text{C}] = kK[\text{N}_0][\text{H}_0] \quad (24)$$

if $[\text{N}_0] \gg [\text{H}_0]$, and $K[\text{N}_0] \gg 1$, $[\text{C}] \approx [\text{H}_0]$

$$\text{rate} = k[\text{H}_0] \quad (25)$$

$$\begin{aligned} \text{if } [H_0] \gg [N_0], K[H_0] \gg 1, [C] \approx [N_0] \\ \text{rate} = k[N_0] \end{aligned} \quad (26)$$

Reaction scheme (*iv*):



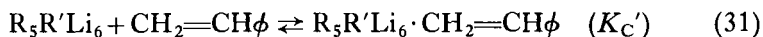
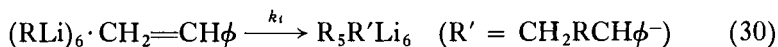
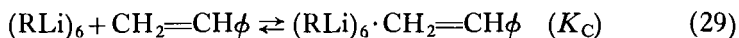
While these four schemes by no means exhaust the possibilities, they represent a broad spectrum of mechanisms in terms of molecularity and polarity of the transition state. Some organolithium reactions, e.g., thermal decomposition, very probably proceed via radical formation. Furthermore, there is evidence that the coupling reaction with an alkyl halide may involve radicals (72), although these systems must be more extensively investigated. Reaction scheme (*iv*) can probably be ruled out immediately; it would require an inordinately high activation energy, would probably lead to a negligible lithium kinetic isotope effect, and would not account for stereospecificity in olefin polymerization (68, 73). It possibly becomes an important pathway, however, in the presence of more polar molecules such as ethers.

Reaction scheme (*i*) has been most widely subscribed to by polymer chemists. In this writer's opinion it is not a likely pathway for reaction. The enthalpy change for dissociation of hexamer into monomer molecules, Eq. (7), is not known, but is probably on the order of 100 kcal/mole of hexamer, at a minimum. This, coupled with an unfavorable entropy effect, should make the free energy change for Eq. (7) so large (positive) that no reasonable assumption about the kinetic behavior of the various candidate species will suffice to make the concentration of monomer rate-determining. It must be recalled that the mass spectral data for ethyllithium vapor at 87° C failed to show the presence of any monomer. Intermolecular exchange of alkyl groups, observed in NMR studies of ethyllithium (47), almost certainly proceeds by dissociation of hexamer into tetramer and dimer. The enthalpy of dissociation of polyisoprenyllithium dimer has been estimated to be about 37 kcal/mole (31*b*). If a similar value obtains for short chain *n*-alkyllithium compounds (and there is reason to believe it does), the rate of formation of monomer could not possibly be as fast as the observed rates of initiation. Finally, it is difficult to see how a monomeric alkyl-lithium species could confer the required stereospecificity in reaction with an olefin (73).

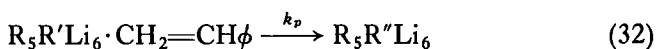
Reaction scheme (ii) is more likely than (i) on energy grounds. The dimer is probably an important species present in ether or triethylamine solutions of *n*-alkyllithium compounds, and might therefore reasonably be expected to function as a reactive intermediate in hydrocarbon solution. Rather complex kinetics should follow from scheme (ii), because various concurrent equilibria between alkyllithium species (e.g., between tetramer and hexamer, tetramer and tetramer, etc.) would be in effect.

Reaction scheme (iii) is preferable in some respects to the others listed. It has been shown that the hexamer acts as a Lewis acid in forming complexes with bases such as lithium ethoxide or triethylamine in solution. Association may be looked for also with less basic nucleophiles such as alkyl halides, olefins, or carbonyl compounds. Depending upon the relative concentrations of alkyllithium compound and substrate N, and upon the magnitude of the equilibrium constant for pre-equilibrium, the apparent order of reaction in either alkyllithium or nucleophile may vary widely. First-order kinetics in both RLi and N are to be expected when the equilibrium constant is small, as it very probably is for alkyl halides. K_C might be larger, however, for olefins. Usually a wide range of olefin/alkyllithium ratio is employed in polymerization studies, so that a variable order in alkyllithium is not surprising.³ In any case, the reported one-sixth order in RLi is open to serious question (71a); significant differences are observed in the apparent reaction order of alkyllithium with styrene, from spectrophotometric as compared with dilatometric data (71b). There is an obvious need for careful studies of the kinetics of reaction of alkyllithium reagents with various model substrates, under conditions of rigorous purity and freedom from lithium alkoxide, lithium halides, or other impurities.

As a final commentary on the kinetics of olefin polymerization, it must be kept in mind in dealing with such systems that the product of the reaction is itself an alkyllithium compound, and that this new compound is no doubt incorporated into a polymeric alkyllithium moiety, e.g.,



³ Reported alkyllithium concentrations are based on monomer; when these values are divided by six, the correct concentration of hexamer is obtained for comparison with the olefin concentration.



After only one of the hexamer sites has undergone reaction, a new hexamer is produced. The new species may undergo reaction at the same site (propagation) or may undergo initiation at one of the remaining original sites, but with a different rate constant. As the number of sites which have undergone reaction increases, dissociation into less-associated polymers may occur to further complicate matters. It is evident that the addition of alkyllithium compounds to olefins constitutes a very complex system, kinetically speaking.

B. The Effect of Bases on Alkyllithium Kinetics

The acceleration of the rates of organolithium reactions resulting from low concentrations of bases such as amines or ethers is very great (54, 60, 72-75). The effect no doubt results from complex formation which labilizes the carbon-lithium bond. Coordination of base also apparently results, as expected, in a more ionic transition state. The stereospecificity of olefin polymerization changes very markedly upon addition of base, and varies with base concentration in a manner which suggests that complex formation is responsible (31, 68, 73).

It is not clear whether a small quantity of added base results in a change in the molecularity of the kinetically active organolithium moiety. It is the writer's opinion that the hexamer (and possibly the tetramer as well) is rendered not more reactive by coordination of base, but less so. It is certainly true in general that coordination of base to a Lewis acid decreases the reactivity of the acid. In the present case, coordination of a base to the hexamer would serve to block the sites at which reaction with a substrate might occur. The increase in reactivity of the alkyllithium compounds with addition of base must therefore be ascribed to the fact that base coordination promotes dissociation of the hexamer. The dissociation product, probably a coordinated dimer in most instances, is presumably more reactive than the hexamer.

Where coordination of a base to the hexamer occurs without dissociation of the hexamer, a lower reactivity should result. Lithium ethoxide, which behaves toward ethyllithium in this way, does have the effect of lowering the rate of ethyllithium reactions in hydrocarbon solution (69). There are

probably other bases [e.g., lithium halides (76) as well as other metal halides and alkoxides] which behave in a similar fashion. Shatenstein and co-workers have recently reported results on the effect of ether on the reaction of butyllithium with butyl bromide (77), which indicate that there is a competition between ether and the alkyl halide. For ether/alkyllithium ratios greater than 0.5, the specific rate constant was found to increase with the concentration of *n*-butyl bromide.

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Organometallic Nitrogen Compounds of Germanium, Tin, and Lead

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I

INTRODUCTION

The organometallic nitrogen chemistry of the Group IV elements, except carbon, is comparatively new. Especially since 1950, knowledge in this field has greatly increased. For silicon the number of known compounds is such that a separate treatment seems desirable (1). Accordingly, only the nitrogen compounds of the remaining elements, germanium, tin, and lead, will be covered here. Also, this review will be limited to organometallic derivatives of amines and amides. Pseudohalides and other types of nitrogen compounds will be mentioned only in passing.

The first organogermylamines and organogermazanes were obtained around 1930 by C. A. Kraus *et al.* The work on the organotin chemistry of analogous compounds having tin—nitrogen bonds started even later, viz. around 1960. Today many metal-nitrogen compounds of both elements are

known. For lead progress has paralleled that for tin, but the number of known lead-nitrogen derivatives is much smaller.

The study of Group IV organometallic nitrogen compounds is interesting from two points of view. First, the metal-nitrogen bond in many cases has a high reactivity. Second, the existence of pentacoordinated tin and lead was demonstrated first with certain types of nitrogen compounds.

II

GERMANIUM

A. Introduction

Around 1930 a few reactions between organogermanium halides and ammonia were studied by Kraus *et al.* (cf. 2). Further progress was slow and even by 1960 less than twenty organogermynes and organogermazanes were known. Meanwhile, some other types of nitrogen containing compounds had been prepared, viz. isocyanides, isocyanates, and isothiocyanates.

The observation that certain types of organotin-nitrogen compounds are pentacoordinated prompted the study of corresponding germanium compounds. However, it appeared that the situation with germanium is different from that for tin and lead (3). Subsequently work was extended to a more general study of the germanium-nitrogen bond.¹

B. The Formation of Germanium-Nitrogen Bonds

1. Earlier Preparative Methods

a. *Reactions of Germanium Halides with Ammonia and Amines.* Germanium tetrahalides and organogermanium halides react with ammonia and with most amines. Initially adducts are formed, but most of these are stable only at temperatures well below zero (4-7). Table I lists the adducts formed by the halogenogermanes which are reported to be stable at room temperature. These compounds will not be discussed here; for a general review of these coordination compounds the reader is referred to a recent review article (8).

¹ Most of the results described here have been published in the doctoral thesis of one of the authors (F. R.), State University of Utrecht, November 1964 (27). Cf. also (117).

TABLE I
ADDUCTS OF HALOGENOGERMANES WITH AMMONIA, HYDRAZINE, AND AMINES WHICH ARE STABLE AT ROOM TEMPERATURE

Ligands	Acceptor molecules						
	GeF ₄	GeCl ₄	GeBr ₄	GeI ₄	H ₃ GeF	(CH ₃) ₃ GeBr	(C ₂ H ₅) ₃ GeBr
Ammonia	1:2 (9, 10)	1:6, 1:16 (13)	—	—	1:1 (7)	1:1 (5, 7)	1:1 (20)
Hydrazine	1:2 (9, 10)	—	—	—	—	—	—
Primary amines							
Methylamine	—	—	—	—	—	1:1 (6)	—
Ethylenediamine	1:1 (9, 10)	—	—	—	—	—	—
Secondary amines							
Dimethylamine	—	—	—	—	—	1:1 (6)	—
Pyrrolidine	1:2 (9)	—	—	—	—	—	—
Piperidine	1:2 (10)	—	—	—	—	—	—
Tertiary amines							
Trimethylamine	1:1, 1:2 (9, 11)	1:1, 1:2 (11)	—	—	—	1:1 (6)	—
Dimethylaniline	1:2 (9, 12)	^a	—	—	—	—	—
Triethylamine	—	1:4 (14)	—	1:5 (19)	—	—	—
Cyclohexylamine	—	—	—	1:4 (13)	—	—	—
Acetonitrile	1:2 (9)	—	—	—	—	—	—
Pyridine	1:2 (9, 10, 12)	1:2 (15, 16, 17, 18)	1:2 (15)	—	—	—	—
2,2'-Bipyridine	—	1:1 (15, 17)	1:1 (15)	—	—	—	—
1,10-Phenanthroline	—	1:1 (17)	1:1 (15)	—	—	—	—
Tetra- <i>N</i> -methylethylene-diamine	—	1:1 (11)	—	—	—	—	—

^a Does not react (21).

Many adducts of halogenogermanes with ammonia or primary or secondary amines react further, even below room temperature, with elimination of quaternary ammonium salts and formation of organogermynes (cf. Table II).



R = H or an organic substituent

Two or more $-\text{NH}_2$ or $-\text{NHR}$ groups linked to one germanium atom are unstable, and tend to decompose to afford compounds of the types $[\text{Ge}(\text{NR})_2]$, $[\text{RGeN}]$, or $[\text{R}_2\text{GeNH}]$ (2, 21).² On the other hand some exceptions exist. From germanium tetrachloride and appropriate amounts of aniline or cyclohexylamine, respectively, Davidson (22) prepared compounds which he formulated as $\text{ClGe}(\text{NHC}_6\text{H}_5)_3$, $\text{Cl}_2\text{Ge}(\text{NHR})_2$ (R = phenyl or cyclohexyl), and $\text{Ge}(\text{NHC}_6\text{H}_{11})_4$. Although the structure of the chlorine-containing compounds may be formulated in an alternative way, there is no reason to doubt the structure of the latter compound.

Partial substitution of chlorine by an amino group has also been observed in the reaction between dimethyldichlorogermane and ammonia in ether, yielding $[(\text{CH}_3)_2\text{GeCl}]_3\text{N}$ in addition to polymeric dimethylgermazanes (23).

In the reaction between compounds of the type R_3GeCl and ammonia, hydrogen chloride is eliminated if R = phenyl. The trialkylchlorogermanes, however, require a stronger hydrogen chloride acceptor than ammonia, for example, an alkali metal (2). In the former reaction $(\text{C}_6\text{H}_5)_3\text{GeNH}_2$ is formed, the only compound known containing a GeNH_2 group. This compound easily loses ammonia, yielding $[(\text{C}_6\text{H}_5)_3\text{Ge}]_2\text{NH}$ or, at elevated temperatures, even $[(\text{C}_6\text{H}_5)_3\text{Ge}]_3\text{N}$ (2). Trialkylchlorogermanes upon treatment with liquid ammonia and an alkali metal yield hexaalkyldigermazanes, $(\text{R}_3\text{Ge})_2\text{NH}$.

If halogen atoms in germanium halides are replaced by alkyl or aryl groups there is a diminished tendency to react with amines. Thus, diethyldibromogermane yields $(\text{C}_2\text{H}_5)_2\text{GeNH}$ with ammonia (2), but triethylbromogermane forms a rather unstable adduct only (20); germanium tetrachloride is completely aminolyzed by ethylamine in contradistinction to diphenyl-

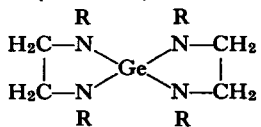
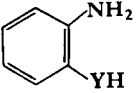
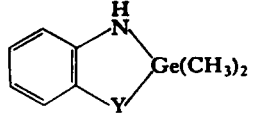
² These compounds doubtless are polymers or cyclic oligomers owing to the absence of $p\pi-p\pi$ double bonding. In the course of our own work $(n\text{-C}_4\text{H}_9)_2\text{GeNH}$ was found to be trimeric.

TABLE II

REACTION PRODUCTS FORMED FROM HALOGENOGERMANES AND AMMONIA OR AMINES ^a

Reactants		Products ^b	References	Remarks
Halogenogermane	Amine			
<i>Reactions with ammonia</i>				
GeCl ₄	NH ₃ liq.	Ge(NH) ₂	2, 13	Or in CCl ₄ with gaseous NH ₃
GeI ₄	NH ₃ liq.	Ge(NH) ₂	19	
C ₂ H ₅ GeI ₃	NH ₃ liq.	C ₂ H ₅ GeN	2	
H ₂ GeCl ₂	NH ₃ liq.	Ge	7	In ether
(CH ₃) ₂ GeCl ₂	NH ₃	[(CH ₃) ₂ GeCl] ₃ N ^c	23	
(C ₂ H ₅) ₂ GeCl ₂	NH ₃ liq.	(C ₂ H ₅) ₂ GeNH	2	In the presence of sodium
(<i>n</i> -C ₄ H ₉) ₂ GeCl ₂	NH ₃ liq.	[(<i>n</i> -C ₄ H ₉) ₂ GeNH] ₃	27	
(C ₆ H ₅) ₂ GeCl ₂	NH ₃ liq.	(C ₆ H ₅) ₂ GeNH	2	In ether
(CH ₃) ₃ GeCl	NH ₃	[(CH ₃) ₃ Ge] ₂ NH	23	
(C ₂ H ₅) ₃ GeBr	NH ₃ liq.	[(C ₂ H ₅) ₃ Ge] ₂ NH	2	In the presence of sodium ^d
(<i>n</i> -C ₄ H ₉) ₃ GeCl	NH ₃ liq.	[(<i>n</i> -C ₄ H ₉) ₃ Ge] ₂ NH	27	In the presence of sodium
(C ₆ H ₅) ₃ GeBr	NH ₃ gaseous	(C ₆ H ₅) ₃ GeNH ₂	2	In organic solvents
<i>Reactions with primary amines</i>				
GeCl ₄	C ₂ H ₅ NH ₂	Ge(NC ₂ H ₅) ₂	2, 21	In the vapor phase or in ether
GeCl ₄	C ₆ H ₅ NH ₂	Ge(NC ₆ H ₅ ·HCl) ₂	21, 22	In ether or benzene
GeCl ₄	C ₆ H ₁₁ NH ₂	Ge(NC ₆ H ₁₁ ·HCl) ₂	22	In benzene
GeCl ₄	C ₆ H ₅ NH ₂ (excess)	ClGe(NHC ₆ H ₅) ₃	22	In boiling benzene

TABLE II—*continued*

Reactants		Products ^b	References	Remarks
Halogenogermane	Amine			
GeCl ₄	C ₆ H ₁₁ NH ₂ (excess)	Ge(NHC ₆ H ₁₁) ₄	22	In boiling benzene
GeCl ₄	RHNCH ₂ CH ₂ NHR R = CH ₃ , C ₂ H ₅ , C ₆ H ₅ , p-CH ₃ C ₆ H ₅		28	In benzene
GeI ₄	C ₂ H ₅ NH ₂ liq.	Ge(NC ₂ H ₅) ₂	19	In liquid ethylamine or in CCl ₄
(CH ₃) ₂ GeCl ₂	CH ₃ NH ₂	[(CH ₃) ₂ GeNCH ₃] ₃	29	In ether
(CH ₃) ₂ GeCl ₂	 Y = NH, O or S	 Y = NH, O or S	24, 25	In the presence of triethylamine
(C ₆ H ₅) ₂ GeCl ₂	C ₂ H ₅ NH ₂	Only slight, if any, aminolysis	2	
H ₃ GeCl	CH ₃ NH ₂ liq.	(GeH ₂) _x	5	
<i>Reactions with secondary amines</i>				
GeCl ₄	C ₅ H ₁₀ NH	Ge(NC ₅ H ₁₀) ₄	21	In ether
GeCl ₄	(C ₂ H ₅) ₂ NH	Ge(NC ₂ H ₅) ₂ · HCl	21	In the vapor phase or in ether
GeCl ₄	Phthalocyanine	PcGeCl ₂ ^e	30, 31, 32	In the presence of quinoline
GeCl ₄	2-Cyanobenzamide	PcGeCl ₂ ^e	31	In the presence of 1-chloro-naphthalene

GeBr ₄	(CH ₃) ₂ NH	Ge[N(CH ₃) ₂] ₄	4	In cyclohexane
GeBr ₄	(C ₂ H ₅) ₂ NH	Ge[N(C ₂ H ₅) ₂] ₄	4	In cyclohexane
GeI ₄	(C ₂ H ₅) ₂ NH liq.	Aminolysis ^f	19	
C ₂ H ₅ GeCl ₃	(CH ₃) ₂ NH	C ₂ H ₅ Ge[N(CH ₃) ₂] ₃	4	In cyclohexane
C ₂ H ₅ GeCl ₃	(C ₂ H ₅) ₂ NH	C ₂ H ₅ Ge[N(C ₂ H ₅) ₂] ₃	4	In benzene
(<i>n</i> -C ₄ H ₉) ₂ GeCl ₂	(CH ₃) ₂ NH	(<i>n</i> -C ₄ H ₉) ₂ Ge[N(CH ₃) ₂] ₂	26	In hexene
H ₃ GeCl	(CH ₃) ₂ NH liq.	(GeH ₂) _x	33	
<i>Reactions with tertiary amines</i>				
H ₃ GeCl	(CH ₃) ₃ N liq.	(GeH ₂) _x	7	
H ₃ GeCl	C ₅ H ₅ N	(GeH ₂) _x	7	

^a Cf. Table I for reactions in which adducts are formed only.

^b The quaternary ammonium salts obtained are omitted.

^c Also polymeric dimethylgermazanes are formed.

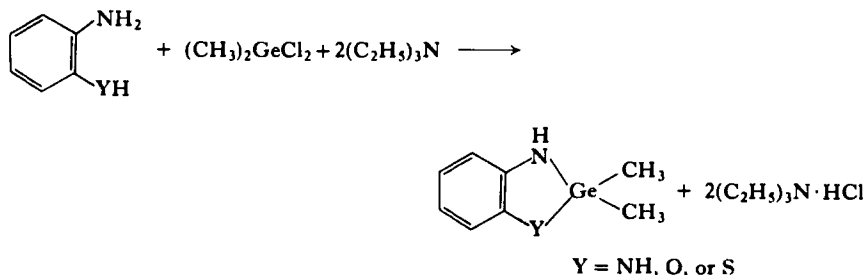
^d Without sodium only a rather unstable adduct is formed (20).

^e Pc = the phthalocyanyl group. From this compound also PcGeX₂ (X = other halogens, OH, OR, or OSiR₃) were prepared.

^f Products were not characterized.

dichlorogermane (2); the latter compound yields $(C_6H_5)_2GeNH$ upon reaction with ammonia (2).

On the other hand, complete aminolysis of dimethyldichlorogermane can occur in the presence of triethylamine as a hydrogen chloride acceptor (24, 25).

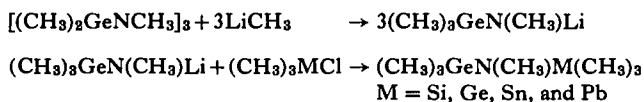


Reactions between germanium tetrachloride, alkyltrichlorogermane, or dialkyldichlorogermane and secondary amines in petroleum ether yield compounds of the type $Ge(NR_2)_4$, $RGe(NR_2)_3$, and $R_2Ge(NR_2)_2$, respectively (4, 26).³ With tertiary amines the germanium halides either do not react or form adducts (cf. Table I).

In Table II reactions between halogenogermanes and ammonia or amines are summarized.

b. Other Reactions by Which a Germanium-Nitrogen Bond is Formed.

In a few cases halogermanes have been treated with alkali metal derivatives of amines. Moreover, recently (29) an alkali metal derivative of a germylamine has been found to react with Group IV organometallic chlorides.



Compounds prepared by both types of reactions are listed in Table III.

In principle alkali metal derivatives of germanes can be converted to compounds containing a germanium-nitrogen bond. This synthetic method is of a very limited scope since trialkylgermyl-alkali metal compounds can

³ These results are at variance with earlier work (21) which reported the formation of $Ge(NC_2H_5)_2 \cdot HCl$ from the reaction between germanium tetrachloride and diethylamine in the vapor phase or in ether.

TABLE III
COMPOUNDS PREPARED BY REACTION OF HALOGENOGERMANES
WITH ALKALI METAL DERIVATIVES OF AMINES

Compound	References	Compound	References
$\text{Ge}(\text{NC}_4\text{H}_4)_4^a$	34	$(n\text{-C}_4\text{H}_9)_3\text{GeN}(\text{C}_2\text{H}_5)_2$	27
$(\text{CH}_3)_2\text{Ge}\{\text{N}[\text{Si}(\text{CH}_3)_3]_2\}$	35	$(n\text{-C}_4\text{H}_9)_3\text{GeNC}_4\text{H}_4^a$	27
$(n\text{-C}_4\text{H}_9)_2\text{Ge}(\text{NC}_4\text{H}_4)_2^a$	27	$(n\text{-C}_4\text{H}_9)_3\text{GeNC}_6\text{H}_5^b$	27
$(\text{CH}_3)_3\text{GeN}(\text{CH}_3)\text{Si}(\text{CH}_3)_3$	29	$(n\text{-C}_4\text{H}_9)_3\text{GeNC}_4\text{H}_4\text{O}_2^c$	27
$(\text{CH}_3)_3\text{GeN}(\text{CH}_3)\text{Ge}(\text{CH}_3)_3$	29	$(n\text{-C}_4\text{H}_9)_3\text{GeNC}_6\text{H}_4\text{O}_2^d$	27
$(\text{CH}_3)_3\text{GeN}(\text{CH}_3)\text{Sn}(\text{CH}_3)_3$	29	$(\text{C}_6\text{H}_5)_3\text{GeNH}_2$	2
$(\text{CH}_3)_3\text{GeN}(\text{CH}_3)\text{Pb}(\text{CH}_3)_3$	29	$(\text{C}_6\text{H}_5)_3\text{GeN}(\text{C}_6\text{H}_5)_2$	38
$(\text{CH}_3)_3\text{GeN}[\text{Si}(\text{CH}_3)_3]_2$	35, 36, 37	$(\text{C}_6\text{H}_5)_3\text{GeNC}_4\text{H}_4^a$	27
$[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{NH}$	2		

^a $\text{NC}_4\text{H}_4 = N\text{-pyrrolyl}$.

^b $\text{NC}_6\text{H}_5 = N\text{-indolyl}$.

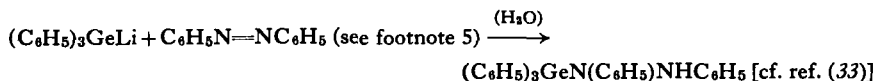
^c $\text{NC}_4\text{H}_4\text{O}_2 = N\text{-succinimidl}$.

^d $\text{NC}_6\text{H}_4\text{O}_2 = N\text{-phthalimidl}$.

not be prepared in satisfactory yields. Two examples, involving different types of reaction, are known.



$\text{R} = \text{H}$ (see footnote 4) or phenyl (39, 40)



Germyllithium, H_3GeLi , forms complexes with ammonia, of which the 1:2 adduct is stable at room temperature (41).

2. New Methods for the Synthesis of Germanium-Nitrogen Bonds: The Preparation of Compounds in Which the Nitrogen Atom is Part of a Heterocyclic System

Because of earlier findings in organotin chemistry (see Section III, E) it was felt desirable to study a series of compounds in which an organo-germanium group is linked to the nitrogen atom of a heterocyclic system

⁴ H_3GeNH_2 has not been isolated.

⁵ Or azoxybenzene which is reduced to azobenzene by another molecule of triphenyl-germyllithium prior to addition.

(27). Moreover, while investigating the properties of these compounds some other types of compounds containing a germanium–nitrogen bond were prepared for comparison purposes. In Table IV the compounds synthesized and the methods of preparation employed are summarized.

TABLE IV

NEW ORGANOGERMANIUM COMPOUNDS CONTAINING A GERMANIUM–NITROGEN BOND^a

Compound	Method of preparation	B.p. (m.p.) (°C/mm)	n_D^{20}	Yield (%)
Hexabutylcyclotrigermazane	<i>g</i>	172°/0.004	1.4889	26
Dibutyl-di- <i>N</i> -pyrrylgermane	<i>b</i>	156°–160°/1.1	1.5222	51
Hexabutylidigermazane	<i>g</i>	144°–146°/0.2	1.4727	88
<i>N</i> -Tributylgermyloctylamine	<i>e</i>	130°–134°/0.06	1.4594	22
<i>N</i> -Tributylgermyldiethylamine	<i>c</i>	84°–88°/0.15–0.20	1.4606	59
<i>N</i> -Tributylgermylpyrrolidine	<i>e</i>	158°–160°/12	1.4729	52
<i>N</i> -Tributylgermylpyrrole	<i>b</i>	110°–114°/0.53	1.4882	68
<i>N</i> -Triphenylgermylpyrrole	<i>b</i>	(198°–199°)	—	66
<i>N</i> -Tributylgermyl-2,4-dimethylpyrrole	<i>e</i>	172°–174°/10	1.4932	65
<i>N</i> -Tributylgermylindole	<i>d</i>	125°–130°/0.0015	1.5364	68
<i>N</i> -Tributylgermylpyrazole	<i>f</i>	105°–109°/0.53	1.4828	52
<i>N</i> -Triethylgermylimidazole	<i>f</i>	155°–156°/13	1.4943	13
<i>N</i> -Tributylgermylimidazole	<i>f</i>	117°/0.07	1.4892	22
<i>N</i> -Tributylgermyl-1,2,4-triazole	<i>f</i>	123°/0.25	1.4825	27
<i>N</i> -Tributylgermysuccinimide	<i>b</i>	177°/2	1.4870	44
<i>N</i> -Tributylgermylphthalimide	<i>b</i>	159°/0.3	1.5208	22
Bis(tributylgermyl)carbodiimide	<i>h</i>	146°–154°/0.003	1.4823	24

^a From ref. (27).

Methods of preparation:

^b R_3GeX ($X = Cl, Br$) or $R_2GeCl_2 + KN \angle$ in toluene.

^c $R_3GeCl + LiN \angle$ in ether.

^d $R_3GeCl + NaN \angle$ in benzene.

^e $(R_3Ge)_2NH + 2HN \angle$ at 160°–170° C.

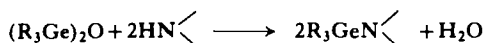
^f $(R_3Ge)_2O + 2HN \angle$ at 150°–170° C, under removal of water by the slow addition of dry toluene.

^g R_3GeCl or R_2GeCl_2 in liquid $NH_3 + Na$.

^h $R_3GeCl + H_2NCN + NaOC_2H_5$ in ether/alcohol.

Most of the nitrogen derivatives involved are very susceptible to hydrolysis, extreme precautions being required to exclude every trace of

moisture. Reactions starting with a halogenogermane involve an inconvenient filtration of the reaction mixture and washing of the precipitate. For the preparation of the most moisture-susceptible compounds, therefore, preference was given to two other types of reactions which can be carried out more simply, viz. transamination reactions and reactions between germoxanes and amines.



Both reactions are new in organogermanium chemistry.

Unlike the corresponding reactions of organotin compounds (42), the release of water from a trialkylgermoxane and imidazole or benzimidazole does not take place with reasonable speed at the boiling point of benzene. The reactions can be made to proceed by a modified azeotropic distillation, viz. by heating a mixture of the reactants at 150°–170° C and by adding from time to time a few drops of toluene. In this way the water produced is swept away by the solvent vapor and the reaction temperature can be maintained at the required level.

The transamination reactions were carried out by refluxing hexabutyl-digermazane in the presence of an amine and a trace of ammonium sulfate as a catalyst. The ammonia escaping through the reflux condenser was carried away by a slow stream of nitrogen and titrated with acid. Both reactions proceed satisfactorily, but yields are sometimes low (cf. Table IV) because the products are very susceptible to hydrolysis and difficult to purify by distillation.

C. The Properties of Compounds Containing a Germanium–Nitrogen Bond

1. The Absence of Strong Association

It was first investigated whether association occurs with the germanium compounds as with the *N*-trialkylstannylimidazoles (see Section III, E, 4). The occurrence of an appreciable degree of association in solution is indicated by a sharp increase in viscosity with increasing concentration (43). When the viscosity of solutions of *N*-tributylgermylimidazole of increasing

concentration was determined, the concentration dependency showed that no appreciable association occurs (Fig. 1). Clearly, the tendency to form coordination compounds is much lower for germanium than for tin.

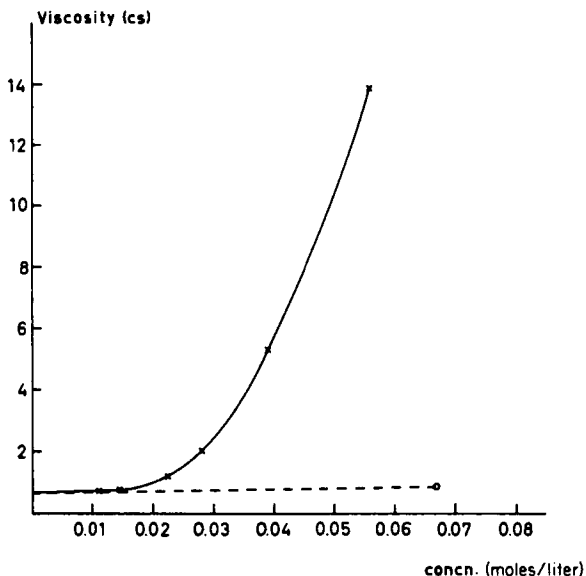
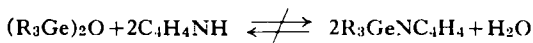


FIG. 1. Viscosity of solutions of *N*-tributylgermyl- and *N*-tributylstannylimidazole in toluene, determined with an *Ubbelohde* (44) viscosimeter at 20°C (the broken and continuous lines, respectively).

2. Cleavage of the Germanium–Nitrogen Bond

In general, germanium–nitrogen compounds are very susceptible to hydrolysis. An exception is the compound $(\text{C}_6\text{H}_5)_3\text{GeN}(\text{C}_6\text{H}_5)\text{NH}(\text{C}_6\text{H}_5)$ which has been isolated in yields of 51–79% after hydrolysis (in the presence of organic solvents) of $(\text{C}_6\text{H}_5)_3\text{GeN}(\text{C}_6\text{H}_5)\text{NLi}(\text{C}_6\text{H}_5)$ with water, or with a saturated aqueous solution of ammonium chloride (33). Remarkable hydrolytic stability has been found for *N*-tributyl- and *N*-triphenylgermylpyrrole. The latter compound can even be dissolved in acetone and precipitated by the addition of water without decomposition. *N*-Tributylgermylpyrrole is not appreciably hydrolyzed upon heating with an equivalent amount of water in a Carius tube at 180°C for 4½ hr. However, the synthesis of these pyrrole derivatives cannot be achieved from the corresponding germoxane and pyrrole. Hexabutyldigermoxane, for instance, does not

react with pyrrole upon heating at 170° C for 4 hr. Thus, even under rather drastic conditions the reaction does not proceed in either direction.



On the other hand, the analogous formation and hydrolysis of the compounds based on the more acidic heterocycles, viz. pyrazole, imidazole, and triazole, proceeds easily. Hydrolysis occurs rapidly at room temperature, and the reverse reaction can be brought about completely or at least to a substantial degree, if much more slowly, by continuous elimination of water above 150° C.

To study these remarkable differences further, the relative reactivity of the germanium–nitrogen bond toward various reagents was determined for a number of structurally related compounds. This was done semiquantitatively by comparing the infrared spectra of solutions (0.5 *M*) of the compound in question in dry benzene and in benzene containing an equivalent amount of the reagent to be investigated.⁶ The following reagents listed in the order of decreasing acidity were studied: phenol, ethyl alcohol, *tert*-butyl alcohol, phenylacetylene, and octylamine. Thus an insight was obtained into the reactivity of the germanium compounds towards a series of reagents, the latter varying from decidedly electrophilic to fairly strongly nucleophilic. The results are compiled in Table V. It follows from these results that the order of reactivity of the reagents corresponds to their acidity and does not follow the order of increasing nucleophilic character.

Apparently the germanium–nitrogen bond in the substituted aliphatic amines and in the substituted heterocycles with more than one nitrogen atom in the ring is very reactive toward reagents with a distinctly acidic character, e.g., phenol and ethyl alcohol. An entirely different behavior was found for tributylgermanium-substituted indole, pyrrole, succinimide, and phthalimide, which are completely stable toward these reagents, or at most react very slowly.

Because the reactivity of the reagents corresponds to their acidic character an electrophilic attack on the nitrogen atom is likely to be the decisive factor. Nucleophilic attack on the germanium atom, though necessarily involved in the reaction, must be much less important since the reactivity of the

⁶ In particular the changes in the 2.5–3.2 μ region which are connected with the disappearance of the alcohols and the formation of the free amines or heterocyclic compounds served as an indication for the occurrence of reaction.

TABLE V
 REACTIVITY OF THE GERMANIUM-NITROGEN BOND IN
 COMPOUNDS OF THE TYPE $(n\text{-C}_4\text{H}_9)_3\text{GeN}<$ TOWARDS EQUIVALENT AMOUNTS
 OF VARIOUS REAGENTS IN BENZENE SOLUTION (0.5 M)

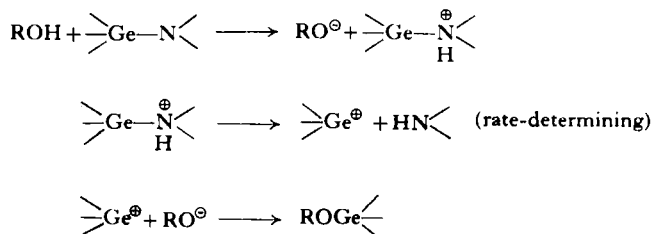
N-containing substituent	Reactivity towards ^a				
	Phenol 1	Ethyl alcohol 2	<i>tert</i> -Butyl alcohol 3	Phenyl- acetylene 4	Octylamine 5
Indole	0	0	—	—	—
Pyrrole	±	0 ^b	—	0	—
Phthalimide	—	0	—	—	—
Succinimide	±	0	—	—	—
2,4-Dimethylpyrrole	+(1-5 hr)	±	—	—	—
Pyrazole	—	++	±	—	0 ^c
Imidazole	—	++	±	0	—
1,2,4-Triazole	++	++	0	0	0
Diethylamine	—	++	—	0	—
Pyrrolidine	—	++	+(< 1 day)	0	+(½ hr)
Order of decreasing acid strength	1	2	3	4	5
Order of increasing nucleophilic properties	2	3/4	3/4	1	5
Order of reactivity	1	2	3	4/5	4/5

^a 0, no reactivity; stable for at least 3 days; ±, very low reactivity, approximately 50% conversion reached after 5 days or longer; +, intermediate reactivity; an indication about the time required for approximately 50% conversion is given between parentheses; ++, very reactive; decomposition completed during the time required to prepare the sample for IR analysis (~1/4 hr).

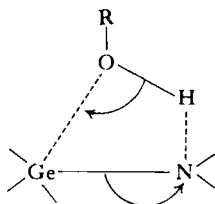
^b Tributylethoxygermane is stable towards pyrrole.

^c *N*-Tributylgermyloctylamine is decomposed within 1/4 hr by pyrazole.

reagents does not parallel their increasing nucleophilic character. The following reaction scheme is suggested:



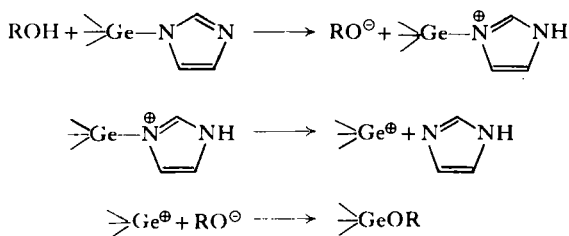
The formation of completely separated charges is not necessary. The reaction may also occur in one step through the following transition state, involving a weak interaction between germanium and oxygen:



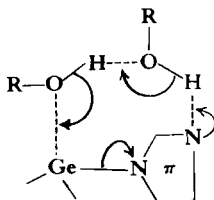
Such a transition state is even more likely because of the low polarity of the solvent (benzene) used.

Electrophilic attack on the nitrogen atom is strongly dependent on the availability of its electron pair. In comparison with the aliphatic amines this availability is decreased when the nitrogen atom belongs to an "aromatic" ring system since the electron pair is delocalized in the π system of the ring (45). This may explain the low reactivity of the pyrrole and indole derivatives.

The high reactivity of the derivatives of pyrazole, imidazole, and triazole is likely to be connected with the presence of the second nitrogen atom. The free electron pair of this nitrogen atom is not involved in the aromatic π system and consequently is very prone to electrophilic attack (46). The probable reaction sequence for these molecules is therefore



Alternatively, when reaction occurs in one step, a transition state, for example,



may be involved. Analogous schemes may be visualized for the pyrazole and triazole derivatives.⁷

It is well known that in succinimide and phthalimide the proton of the imino group has a pronounced acidic character owing to resonance between the nitrogen atom and the neighboring carbonyl groups, thereby markedly reducing the basicity of the nitrogen atom (48). Thus the comparatively low reactivity of the succinimide and phthalimide derivatives may also be understood in terms of a diminished availability of the free electron pair at the nitrogen atom.

As noted at the beginning of this section, *N,N'*-diphenyl(triphenylgermyl)hydrazine (33), $(\text{C}_6\text{H}_5)_3\text{GeN}(\text{C}_6\text{H}_5)\text{NH}(\text{C}_6\text{H}_5)$, shows a marked stability in aqueous media. Probably in this compound also the basicity of the nitrogen atom linked to germanium is lowered by resonance, this time with the phenyl group. The low basicity of anilines, for example, is explained in this way (49).

Summarizing, it has been demonstrated that in general the germanium–nitrogen bond is very reactive toward reagents with a distinct acidic character. In apolar solvents this reactivity is probably due to an electrophilic attack on the free electron pair of the nitrogen atom. Reactivity is considerably lowered for compounds in which the availability of this free electron pair is restricted, e.g., for *N*-tributylgermylpyrrole. The observed high reactivity of *N*-tributylgermyl-substituted heterocycles which contain a second nitrogen atom in the ring may be explained by assuming electrophilic attack on the free electron pair of this atom.

The compounds with a reactive germanium–nitrogen bond readily undergo transamination and substitution reactions with compounds having proton-active hydrogen atoms. In particular the transamination reaction offers a route to many other germanium derivatives. It may be expected, therefore, that the digermazanes will prove to be very suitable intermediates for the preparation of many new compounds.

⁷ After the occurrence of some decomposition the free heterocycles formed, pyrazole, imidazole, or triazole, may take part in the reaction. Since they are more acidic than ethyl alcohol (47) they may protonate the tertiary nitrogen atom of the unreacted molecules, thus facilitating the nucleophilic substitution at the germanium atom by the ethoxy group. An autocatalytic effect therefore might be operative in these reactions.

III

Tin

A. Introduction

The development of organotin–nitrogen chemistry was until recently very slow. The reported synthesis of *N*-triethylstannylurea by Kulmiz (50) in 1860 has never been repeated. Bullard and Robinson (51) in 1927 obtained a mixture of trimethylphenyltin and tris(trimethylstannyl)amine from trimethyltin-sodium and bromobenzene in liquid ammonia, but they were unable to isolate the tin-amine. Between 1950 and 1960 a number of organotin-substituted carbonimides and sulfonamides were described. Moreover, a large number of organotin complexes became known in which nitrogen is coordinated to tin. Before 1960, however, not a single compound of the general formula $R_n\text{Sn}(\text{NR}'\text{R}'')_{4-n}$ was known.

The first representative of this class, tetrakis(diethylamino)tin, $\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_4$, was described in 1961 (52). The reagent used in its preparation, $\text{LiN}(\text{C}_2\text{H}_5)_2$, afterwards proved to be equally suited to the preparation of other organotin amine derivatives.

In 1962 the field of organotin amine chemistry was at last opened up with the publication of four papers (53, 54, 55, 56) on the preparation of compounds of general formula $R_n\text{Sn}(\text{NR}'\text{R}'')_{4-n}$ covering all possibilities from $n = 0$ to $n = 3$. In one of these papers (56), moreover, compounds with more than one tin atom joined to the same nitrogen atom, as well as a cyclic compound of the formula $[\text{R}_2\text{SnNR}']_3$, were described.

Early in the same year the synthesis of compounds in which a triorganotin group is bound to heterocyclic nitrogen was announced (42). In contrast to the organotin amine derivatives, these are very stable to moisture provided a second nitrogen occurs at the 3-position with respect to the first in the heterocyclic ring. It was shown that this is due to a stabilization of the crystalline state through pentacoordination around the tin atom.

More recently, organotin azides and tin derivatives of hydrazine, 1,3-diphenyltriazene, formamide, urea, isourea, guanidine, amidine, carbo-diimide, carbamic, and thiocarbamic acids, an imidoether and imido-phosphoranes have been prepared, so that now almost every imaginable type of organotin–nitrogen compound has become known.

B. Complex Compounds

Complex compounds are formed by treating organotin halides with ammonia or amines. Those described in the literature up to 1960 have been

summarized (57). It appears that halides of the types $R\text{SnX}_3$ and $R_2\text{SnX}_2$ generally combine with 2 moles, and halides of the type $R_3\text{SnX}$ with 1 or 2 moles of ammonia or amines. The structure of these compounds has long remained uncertain (58, 59, 60). Thomas and Rochow (61) were the first to suggest that tin is able to expand its valence shell, whereas carbon cannot. This implies that both the halogen atom and the nitrogen atom are covalently bound to tin. This idea has been confirmed for the trimethyltin chloride-pyridine complex by Beattie, McQuillan, and Hulme (62). Results of infrared measurements and X-ray analysis point to a trigonal bipyramidal pentacoordinate arrangement of ligands around the tin atom. The trimethyltin group is planar and the chlorine atom and the pyridine molecule lie on either side of the plane (63). Complexes formed between amines and the organotin halides $R_2\text{SnX}_2$ and $R\text{SnX}_3$ are probably six-coordinate.

Recently complexes of diorganotin dihalides with bidentate ligands like 2,2'-bipyridyl and 1,10-phenanthroline have been described. These are in general well-crystallized solids with sharp melting points. They are hydrolytically much more stable than the complexes with monodentate ligands and are suited to the characterization and isolation of diorganotin dihalides. In these complexes the tin atom is presumably again six-coordinated. This is true also for the diorganotin dioxinates, a few of which

TABLE VI
ORGANOTIN CHELATE COMPLEXES

Compound	M.p. (°C)	References
$(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{bipy}^a$	240°	67
	232°–233°	68
$(\text{C}_2\text{H}_5)_2\text{SnCl}_2 \cdot \text{bipy}$	200°–201°	69, 70
	195°–196°	68
$(n\text{-C}_3\text{H}_7)_2\text{SnCl}_2 \cdot \text{bipy}$	204°–205°	68
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2 \cdot \text{bipy}$	179.5°–180°	71
	180° ^e	69, 70
	177°–179°	68
$(n\text{-C}_4\text{H}_9)_2\text{SnBr}_2 \cdot \text{bipy}$	176°–177°	69, 70
$(n\text{-C}_4\text{H}_9)_2\text{SnI}_2 \cdot \text{bipy}$	163°	69, 70
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{CNS})_2 \cdot \text{bipy}$	152.5°–153°	70
$(n\text{-C}_8\text{H}_{17})_2\text{SnCl}_2 \cdot \text{bipy}$	133°–133.5°	70
$(\text{C}_6\text{H}_5)_2\text{SnCl}_2 \cdot \text{bipy}$	243°–245°	69, 70
	239°–240°	68

TABLE VI—continued

Compound	M.P. (°C)	References
$\text{CH}_3\text{SnCl}_3 \cdot \text{bipy}$	—	67
$n\text{-C}_4\text{H}_9\text{SnCl}_3 \cdot \text{bipy}$	227°–228°	70
$t\text{-C}_4\text{H}_9\text{SnBr}_3 \cdot \text{bipy}$	> 300°	70
$(\text{CH}_3)_2\text{SnCl}_2 \cdot \text{phenan}^b$	284°	67
	(dec 200°)	68
$(\text{C}_2\text{H}_5)_2\text{SnCl}_2 \cdot \text{phenan}$	235°–236°	69, 70
	230°–231°	68
$(n\text{-C}_4\text{H}_9)_2\text{SnCl}_2 \cdot \text{phenan}$	200°	69, 70
$(n\text{-C}_4\text{H}_9)_2\text{SnBr}_2 \cdot \text{phenan}$	199°–201°	69
	199°–200°	70
$(n\text{-C}_4\text{H}_9)_2\text{SnI}_2 \cdot \text{phenan}$	234°–236°	70
$(n\text{-C}_8\text{H}_{17})_2\text{SnCl}_2 \cdot \text{phenan}$	101°	70
$(\text{C}_6\text{H}_5)_2\text{SnCl}_2 \cdot \text{phenan}$	235° (dec)	69, 70
$\text{CH}_3\text{SnCl}_3 \cdot \text{phenan}$	—	67
$(\text{CH}_3)_2\text{Sn}(\text{oxin})_2^c$	236.5°–238°	72
	231°–233°	68
$(\text{C}_2\text{H}_5)_2\text{Sn}(\text{oxin})_2$	177°–178°	72
	167°–168°	68
$(n\text{-C}_3\text{H}_7)_2\text{Sn}(\text{oxin})_2$	162°–163°	72
	151°–153°	68
$(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{oxin})_2$	154.5°–155.5°	71
	155°–156°	72
	150°–152°	68
$(i\text{-C}_4\text{H}_9)_2\text{Sn}(\text{oxin})_2$	188°–189°	72
$(n\text{-C}_8\text{H}_{17})_2\text{Sn}(\text{oxin})_2$	78°–79°	72
$(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Sn}(\text{oxin})_2$	118°–120°	72
$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{oxin})_2$	231°–233°	71
	—	65
	251°–252°	68
$[(\text{C}_6\text{H}_5)_2\text{Sn}][(\text{CH}_2=\text{CH})_3\text{Sn}]_2(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)^d$	—	73
$[(\text{C}_6\text{H}_5)_2\text{Sn}]\text{H}_2(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)$	—	74

^a bipy = 2,2'-bipyridyl.^b phenan = 1,10-phenanthroline.^c oxin = 8-hydroxyquinolate.^d $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8$ = ethylenediaminetetraacetate.^e Sublimes at 140° C/0.01 mm.

have been prepared in recent years. Triphenyltin oxinate has also been prepared. Its UV spectrum in alcoholic solution indicated no chelation for the oxine and tetrahedral coordination at tin (64, 65). However, West *et al.* (66) found that in isooctane the spectrum observed is that expected for the chelated oxine, indicating that the tin is five-coordinate.

The organotin chelate complexes with tin-nitrogen bonds are listed in Table VI. Included are a few complexes of ethylenediaminetetraacetic acid described recently.

C. Substituted Amines

1. Nomenclature

Wiberg *et al.* (53, 75, 76) only prepared compounds with one tin atom per molecule. They regard these compounds as substituted metal amides. Some examples of their nomenclature are given here:



Jones and Lappert (56, 77) favor an organic nomenclature and call the first of these compounds dimethylaminotrimethylstannane. As the term "amide" suggests the presence of a $-\text{C}(\text{O})\text{N}<$ group and may cause confusion with compounds such as the substituted formamides to be discussed later, the present authors favor the organic nomenclature but, in accordance with present usage, prefer the ending "tin" to "stannane." The organic nomenclature is equally suited to denote compounds with more than one tin atom joined to the same nitrogen atom. In this case, however, since the organotin radical is regarded as a substituent, the ending "stannyl" is preferred to "tin."

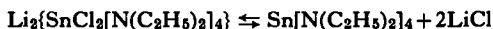
2. Preparation

Tin compounds of the general formula $\text{R}_n\text{Sn}(\text{NR}'_2)_{4-n}$, in contradistinction to the corresponding compounds of silicon and germanium, cannot be prepared by aminolysis of tin tetrahalides or organotin halides. This is due to the fact that in the case of tin the initially formed complex compounds are highly stable. The above compounds are, however, formed in good yields from organotin halides and lithium dialkylamides. Rieger (75) assumes a

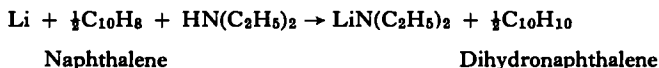
stepwise replacement of halogen atoms by dialkylamino groups via complex formation, e.g.,



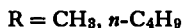
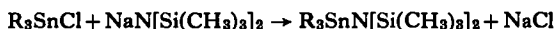
and eventually



Ether was used as a solvent, but an increase in yield was observed if toward the end of the reaction *n*-pentane was added. The latter solvent does not favor formation of polar complexes and, moreover, leads to precipitation of lithium chloride. Schmid has reported that during the preparation of lithium dialkylamides in ether, ether cleavage occurs with formation of lithium ethoxide (76). This gives rise to impurities which are difficult to remove. For the preparation of lithium diethylamide the use of the free amine as a solvent is recommended (76). The over-all reaction is represented by

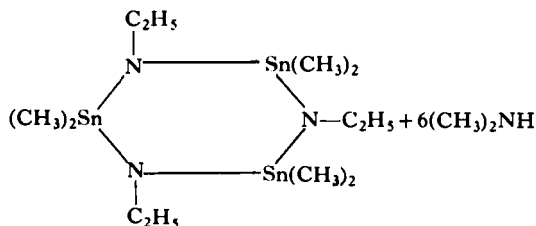
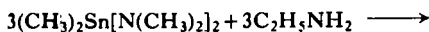
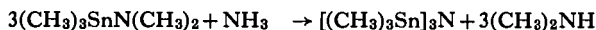
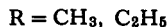
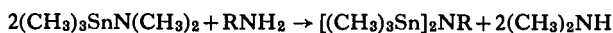


The solvent and dihydronaphthalene are removed by distillation in high vacuum, and the remaining lithium diethylamide is used as a suspension in petroleum ether. Several other metal amides were tried, but lithium diethylamide is superior both to sodium and potassium diethylamide. When these three reagents were used the yields of diethylaminotrimethyltin amounted to 65, 35, and 17%, respectively (76). Silylstannylamines have also been prepared from trialkyltin chlorides and sodium bis(trimethylsilyl)amide (35).



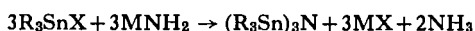
Diethylaminomagnesium bromide, prepared from ethylmagnesium bromide and diethylamine in tetrahydrofuran, can also be used as an aminating reagent (55). In a few cases a transamination reaction has been used to replace a diethylamino group already bound to tin by another amino group (76). Since in this transamination reaction diethylamine is removed by distillation, only heavier groups than diethylamine can be introduced by this method. Starting from diethylaminotributyltin Schmid in this way prepared diphenylaminotributyltin and *N,N'*-bis(tributylstannyl)hydrazobenzene.

Transamination reactions have also been used (56) to prepare compounds in which several tin atoms are bound to the same nitrogen atom, e.g.



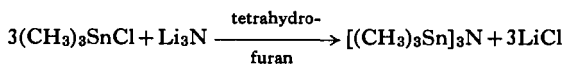
These transamination reactions differ from the foregoing in that secondary amines are displaced by primary amines or by ammonia. They are controlled by steric factors rather than by volatility (56a).

Compounds of the general formula $(\text{R}_3\text{Sn})_3\text{N}$ have also been prepared by Sisido and Kozima (78) who used trialkyltin halides and lithium amide (in liquid ammonia, ether, or tetrahydrofuran) or sodamide (in liquid ammonia).

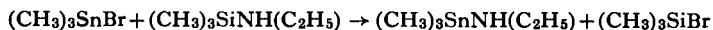


Sodamide in liquid ammonia has also been employed to convert bis(trimethyltin) oxide and trimethyltin phenoxide into tris(trimethylstannyl)amine (79).

In a third method for the preparation of compounds of formula $(\text{R}_3\text{Sn})_3\text{N}$, lithium nitride is used. A reaction between this compound and organotin halides was first noted in 1961 (80), but the first compound prepared by this method, tris(trimethylstannyl)amine, was isolated only in 1964 (81).

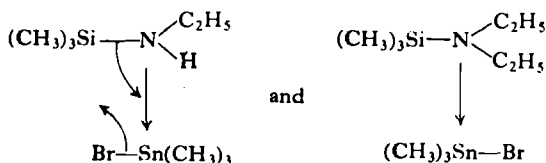


A few less general methods of preparation remain to be mentioned. One is an exchange reaction between silicon and tin, the net result of which is given by

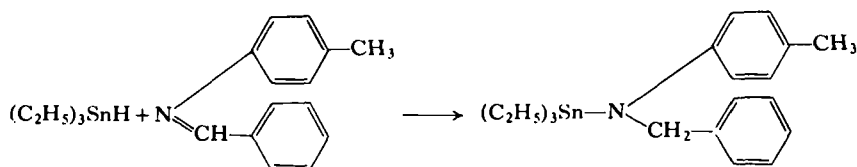


In this reaction a crystalline complex was first formed, which when heated turned into an oil, bromotrimethylsilane being evolved. The corresponding

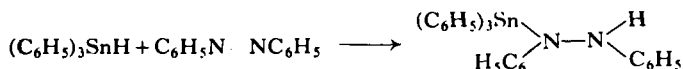
reaction with diethylaminotrimethylsilane did not proceed because of the extreme stability of the initially formed complex (m.p. 203° – 206° C; sublimes *in vacuo* without decomposition). Abel *et al.* (54) explain this difference on steric grounds. Compare



In the addition reaction between triethyltin hydride and *N*-benzyliden-*p*-toluidine, benzyl-*p*-tolylaminotriethyltin is formed (82, 83).

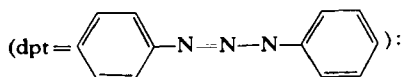
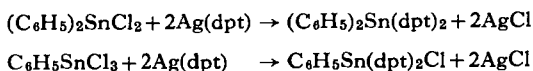


Another addition reaction leading to an organotin-substituted amine was discovered by Noltes (84). From triphenyltin hydride and azobenzene, *N*-triphenylstannyl-*N,N'*-diphenylhydrazine was obtained in good yield.



The corresponding addition product of triethyltin hydride could not be isolated, although its formation was demonstrated by infrared studies and hydrolysis experiments.

An easy method for preparing 1,3-diphenyltriazene derivatives has recently been reported (85). Anhydrous stannic chloride or organotin chlorides are shaken with a slight excess of 1,3-diphenyltriazenido-silver in dry ether. The maximum number of 1,3-diphenyltriazenyl groups introduced in this way is two, e.g.,



The known substituted amines are summarized in Table VII.

TABLE VII
ORGANOTIN-SUBSTITUTED AMINES

Compound	M.p. (°C)	B.p. (°C/mm)	References
$R_n\text{Sn}[\text{N}(\text{CH}_3)_2]_{4-n}$			
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	—	126°/760	56
	—	—	53
	-79°	128°/710	75
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{CH}_3)_2$	—	76°/9	56
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{CH}_3)_2$	—	86°/0.1	56
$(\text{C}_6\text{H}_5)_3\text{SnN}(\text{CH}_3)_2$	—	166°/0.1	56
$(\text{CH}_3)_2\text{Sn}[\text{N}(\text{CH}_3)_2]_2$	—	138°/760	56
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{N}(\text{CH}_3)_2]_2$	—	72°/0.05	56
$(\text{C}_6\text{H}_5)_2\text{Sn}[\text{N}(\text{CH}_3)_2]_2$	—	128°/0.2	56
$\text{CH}_3\text{Sn}[\text{N}(\text{CH}_3)_2]_3^a$	—	—	53
	—	45°-50°/1	75
$n\text{-C}_4\text{H}_9\text{Sn}[\text{N}(\text{CH}_3)_2]_3$	—	67°/0.1	56
$\text{Sn}[\text{N}(\text{CH}_3)_2]_4$	—	51°/0.15	56
$R_n\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_{4-n}$			
$(\text{CH}_3)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	—	156°	75
	—	—	53
	Liquid	156°-162°/760	78
	—	40°-45°/0.1	76
	—	43°/1	
	—	158°-162°/760	
	—	162° ^b	54
	—	140°/720	86
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	—	114°-117°/23	55
	—	—	53
	-126°	225°	75
$(n\text{-C}_3\text{H}_7)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	—	118°-120°/13	55
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	—	115°-120°/1	75
	—	115°-120°/h.v. ^c	76
	—	124°-134°/8	55
$(\text{C}_6\text{H}_5)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	About 40°	165°-175°/0.1	76
	40°	170°/1	75
	—	120°-130°/1	75
	—	125°/1	75
	40°	165°-170°/0.1	86
$(\text{CH}_3)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	—	80°-83°/0.1	76
	—	65°/0.1	86

TABLE VII—*continued*

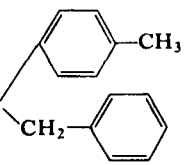
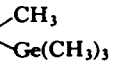
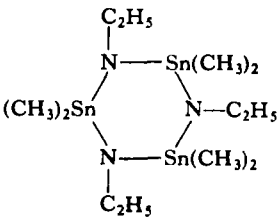
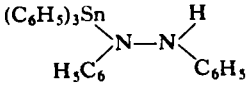
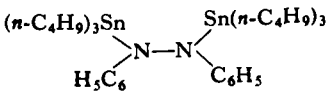
Compound	M.p. (°C)	B.p. (°C/mm)	References
$(C_2H_5)_2Sn[N(C_2H_5)_2]_2$	—	—	53
	-95°	108°/1	75
$(n-C_4H_9)_2Sn[N(C_2H_5)_2]_2$	—	95°-105°/0.1	76
$(C_6H_5)_2Sn[N(C_2H_5)_2]_2$	-95°	160°/1	75
	—	145°-150°/0.1	86
$CH_3Sn[N(C_2H_5)_2]_3$	—	110°-130°/1 ^a }	75
	—	120°/1 ^a	
	—	92°/0.1	86
$n-C_4H_9Sn[N(C_2H_5)_2]_3$	—	115°/1	76
$C_6H_5Sn[N(C_2H_5)_2]_3$	—	—	53
	-92°	128°/1	75
	—	130°/0.1	86
$Sn[N(C_2H_5)_2]_4$	—	110°-116°/0.1	76
	—	90°/0.1	52
	—	116°/1	53, 75
	—	116°/0.1	86
Other $R_nSn(NR'_2)_{4-n}$			
$(CH_3)_3SnN(i-C_3H_7)_2$	—	63°/8	56
$(CH_3)_2SnN[i-C_3H_7]_2$	—	66°/0.05	56
$(CH_3)_2SnN(n-C_4H_9)_2$	—	74°/2.5	56
$(CH_3)_2SnN(C_6H_5)_2$	—	128°/0.1	56
$(n-C_4H_9)_3SnN(C_6H_5)_2$	—	170°-175°/0.1	76
$(CH_3)_2SnN[Si(CH_3)_3]_2$	20°-22°	58°-59°/1	35
$(n-C_4H_9)_3SnN[Si(CH_3)_3]_2$	—	140°-145°/1	35
$R_3SnNR'R''$			
$(CH_3)_3SnNH(C_2H_5)$	—	153° ^d	54
$(CH_3)_3SnNH(C_6H_5)$	—	77°/0.05	56
$(CH_3)_3SnN(CH_3)(C_6H_5)$	—	82°/0.1	56
$(C_2H_5)_3SnN$ 	—	142°/0.001	83
$(CH_3)_3SnN$ 	—	28°/2	29

TABLE VII—continued

Compound	M.p. (°C)	B.p. (°C/mm)	References
(R ₃ Sn) ₂ NR'			
[(CH ₃) ₃ Sn] ₂ NCH ₃	—	64°/3	56
[(CH ₃) ₃ Sn] ₂ NC ₂ H ₅	—	93°/15	56
(R ₃ Sn) ₃ N			
[(CH ₃) ₃ Sn] ₃ N	22°–24°	133°–134°/20	78
	—	130°/14	
	—	70°/0.2	
	—	84°/0.40	
	26°–28°	—	79
[(C ₂ H ₅) ₃ Sn] ₃ N	21°–22°	192°–194°/4	78
[(<i>n</i> -C ₃ H ₇) ₃ Sn] ₃ N	Liquid	143°–145°/0.6	78
Cyclic [R ₂ SnNR'] ₃			
	—	104°/0.05	56
1,2-Diphenylhydrazine derivatives			
	About 130°	—	84
	Oil	—	76
1,3-Diphenyltriazene derivatives			
(C ₆ H ₅) ₃ Sn[N(C ₆ H ₅)N=N(C ₆ H ₅)]	85°	—	85
(CH ₃) ₂ Sn[N(C ₆ H ₅)N=N(C ₆ H ₅)] ₂	164°	—	85
C ₆ H ₅ Sn[N(C ₆ H ₅)N=N(C ₆ H ₅)] ₂ Cl	203°	—	85
Sn[N(C ₆ H ₅)N=N(C ₆ H ₅)] ₂ Cl ₂	190°	—	85

^a Not pure.^b n_D^{20} = 1.4651.^c High vacuum (rotating oil pump).^d n_D^{20} = 1.4689.

3. Properties and Reactions

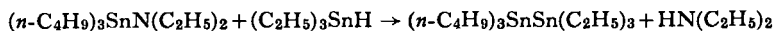
The organotin amine compounds, with a few exceptions, are liquids. They are extremely sensitive toward moisture; when exposed to the air they immediately liberate amine or ammonia. Thermal stability on the other hand is good. Most compounds can be distilled without decomposition. From NMR studies it has been concluded (86) that the tin–nitrogen bond in diethylaminotin compounds is purely covalent.

The tin–nitrogen bond is highly reactive, not only towards water, but also towards many other compounds. Thus tetraisopropoxytin has been prepared from tetrakis(diethylamino)tin and isopropanol in benzene (52). Schmid (76) systematically investigated the reactions of diethylaminotin compounds with compounds containing positive or negative hydrogen. This work has been extended by Jones and Lappert (77, 77a) who moreover mention some addition reactions (56, 77, 77b).

Kula *et al.* (87) have thoroughly studied the reactivity of the tin–nitrogen bond in diethylaminotin compounds toward hydrides. Whereas no reaction is reported to occur with the nucleophiles lithium hydride, sodium borohydride, or lithium aluminum hydride (76), Kula *et al.* observed cleavage of the tin–nitrogen bond by dibutylaluminum hydride and by diborane with formation of organotin hydrides. These workers conclude that for the stability of the tin–nitrogen bond $d_{\pi}-p_{\pi}$ bonding is decisive. If, as is the case in the reaction with dibutylaluminum hydride and diborane, the lone electron pair of the nitrogen is attacked by an electrophilic reagent the tin–nitrogen bond is broken.

Hydrogenolysis of the tin–nitrogen bond in *N*-triphenylstannyl-*N,N'*-diphenylhydrazine by triphenyltin hydride has been observed (84). In this case hexaphenylditin and hydrazobenzene were formed.

Very recently a number of ditin and tritin compounds and some cyclic polytin compounds have been prepared from diethylaminotin compounds and organotin hydrides (88).



This reaction closely resembles that between (*N*-phenylformamido)tin compounds and organotin hydrides (see Section III, D).

In studies of the thermal decomposition of some diethylaminotin compounds it was found that pure diethylaminotrimethyltin is stable up to 300° C (76). The addition of a trace of lithium diethylamide, however, caused severe decomposition at 250° C. Bis(diethylamino)dimethyltin is less

stable. The pure compound decomposes above 270° C with the formation of diethylamine, tetramethyltin, tin, and polymeric products.

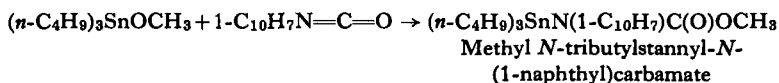
A summary of the reactions of organotin amine compounds is given in Table VIII.

D. Substituted Amides and Related Compounds

The oldest known compounds coming under this heading are organotin sulfonamides and organotin-substituted imides. In 1952 a patent appeared (89) describing the preparation of compounds of the general formula $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{NRSO}_2\text{R}')_2$. These were obtained from the reaction between dibutyltin dichloride and the sodium derivatives of sulfonamides. One tributyltin compound was mentioned as well, viz. tributyltin *N*-ethyl-*p*-toluenesulfonamide. The compounds were claimed to be heat stabilizers for halogen-containing resins, e.g., polyvinyl chloride. Triethyltin methane-sulfonamide and *p*-toluenesulfonamide have been prepared in a similar way (90).

Related to the above-mentioned compounds, in the sense that they contain a tin atom linked to an "acid" nitrogen atom, are *N*-triethylstannylphthalimide and *N*-triethylstannylsaccharin prepared directly from triethyltin hydroxide and phthalimide or saccharin, respectively (91). All these compounds are reasonably stable to hydrolysis. They can be kept in contact with the atmosphere without decomposition.

Addition reactions of organotin alkoxides and distannoxanes with compounds containing multiple carbon-nitrogen bonds affording a variety of organotin-nitrogen compounds have been reported (92). The first reactions of this kind studied were additions of trialkyltin alkoxides to alkyl and aryl isocyanates, e.g.,



The reaction of tributyltin methoxide with isothiocyanate was reported to lead to the corresponding thiocarbamate. It is worthy of note that the adduct of triethyltin hydride and phenyl isothiocyanate contains a tin-sulfur rather than a tin-nitrogen bond (93, 94).

All the above reactions proceed exothermally at room temperature. The reaction products are sensitive to protic reagents. Alcohols cleave the tin-nitrogen bond with regeneration of organotin alkoxide. On this basis the

TABLE VIII
REACTIONS OF ORGANOTIN-SUBSTITUTED AMINES

Tin amine compound	Reagent	Product	Yield (%)	References
$\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_4$	$(\text{CH}_3)_2\text{CHOH}$	$\text{Sn}[\text{OCH}(\text{CH}_3)_2]_4$	75	52
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	HCl	$(n\text{-C}_4\text{H}_9)_3\text{SnCl}$	—	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	HN_3	$(n\text{-C}_4\text{H}_9)_3\text{SnN}_3$	85	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$\text{C}_2\text{H}_5\text{OH}$	$(n\text{-C}_4\text{H}_9)_3\text{SnOC}_2\text{H}_5$	98	76
$(\text{CH}_3)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	$\text{C}_2\text{H}_5\text{OH}$	$(\text{CH}_3)_2\text{Sn}(\text{OC}_2\text{H}_5)_2$	97	76
$n\text{-C}_4\text{H}_9\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_3$	CH_3OH	$n\text{-C}_4\text{H}_9\text{Sn}(\text{OCH}_3)_3^a$	92	76
$(\text{CH}_3)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	$\text{CH}_2\text{OHCH}_2\text{OH}$	$[(\text{CH}_3)_2\text{SnOCH}_2\text{CH}_2\text{O}]_n$	97	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$\text{C}_6\text{H}_5\text{OH}$	$(n\text{-C}_4\text{H}_9)_3\text{SnOC}_6\text{H}_5$	73	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$\text{CH}_3\text{CH}_2\text{COOH}$	$(n\text{-C}_4\text{H}_9)_3\text{SnOCOCH}_2\text{CH}_3$	70	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$\text{CH}_3(\text{CH}_2)_{11}\text{SH}$	b	—	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	$(n\text{-C}_4\text{H}_9)_3\text{SnSCH}_2\text{C}_6\text{H}_5$	85	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$(\text{C}_6\text{H}_5)_2\text{NH}$	$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_6\text{H}_5)_2$	65	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$\text{C}_6\text{H}_5\text{NHNHC}_6\text{H}_5$	$ \begin{array}{c} \text{H}_5\text{C}_6 \\ \diagdown \\ \text{N} - \text{N} \\ \diagup \quad \diagdown \\ (n\text{-C}_4\text{H}_9)_3\text{Sn} \quad \text{Sn}(\text{C}_4\text{H}_9\text{-}n)_3 \end{array} $	88	76
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	$\text{C}_6\text{H}_5\text{NHNHC}_6\text{H}_5$	b	—	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$\text{CH}_2(\text{CN})_2$	b	—	76
$(n\text{-C}_4\text{H}_9)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	H_2 and Pt black or PdCl_2	c	—	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	LiH or NaBH_4	c	—	76
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	LiAlH_4	$(n\text{-C}_4\text{H}_9)_3\text{SnH}$	d	76
$(\text{CH}_3)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	$(n\text{-C}_4\text{H}_9)_2\text{AlH}$	$(\text{CH}_3)_3\text{SnH}$	99	87

TABLE VIII—continued

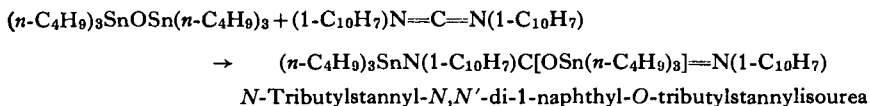
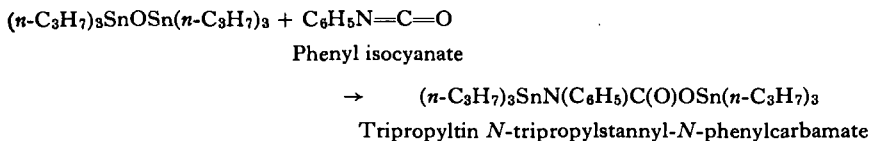
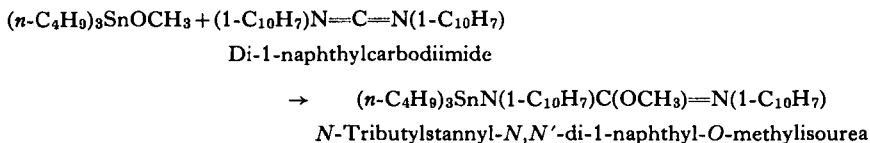
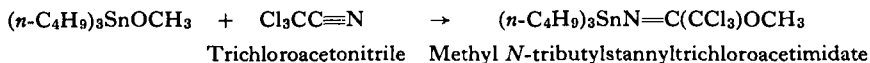
Tin amine compound	Reagent	Product	Yield (%)	References
$(\text{CH}_3)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	$(n\text{-C}_4\text{H}_9)_2\text{AlH}$	$(\text{CH}_3)_2\text{SnH}_2$	42.6	87
$\text{CH}_3\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_3$	$(n\text{-C}_4\text{H}_9)_2\text{AlH}$	CH_3SnH_3	29.1	87
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	B_2H_6	$(\text{CH}_3)_3\text{SnH}$	78.2	87
$(\text{CH}_3)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	B_2H_6	$(\text{CH}_3)_2\text{SnH}_2$	98.4	87
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	B_2H_6	$(n\text{-C}_4\text{H}_9)_3\text{SnH}$	94.4	87
$(\text{C}_6\text{H}_5)_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	B_2H_6	$(\text{C}_6\text{H}_5)_2\text{SnH}_2$	33.5	87
$\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_4$	B_2H_6	SnH_4	20.0	87
$ \begin{array}{c} (\text{C}_6\text{H}_5)_3\text{Sn} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\ \diagdown \quad \diagup \\ \text{H}_5\text{C}_6 \quad \text{C}_6\text{H}_5 \end{array} $	$(\text{C}_6\text{H}_5)_3\text{SnH}$	$(\text{C}_6\text{H}_5)_3\text{SnSn}(\text{C}_6\text{H}_5)_3$	94	84
$\text{R}_3\text{-}_2\text{Sn}[\text{N}(\text{C}_2\text{H}_5)_2]_{1-2}$	$\text{R}_3\text{-}_2\text{SnH}_{1-2}$	Di-, tri-, and polytin compounds	> 65	88
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$(\text{C}_6\text{H}_5)_2\text{AsH}$	$(\text{CH}_3)_3\text{SnAs}(\text{C}_6\text{H}_5)_2$	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$(\text{C}_6\text{H}_5)_2\text{PH}$	$(\text{CH}_3)_3\text{SnP}(\text{C}_6\text{H}_5)_2$	<i>e</i>	77
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{CH}_3)_2$	$(\text{C}_6\text{H}_5)_2\text{PH}$	$(\text{C}_2\text{H}_5)_3\text{SnP}(\text{C}_6\text{H}_5)_2$	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	$(\text{CH}_3)_3\text{SnC}\equiv\text{CC}_6\text{H}_5$	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$	$(\text{CH}_3)_3\text{SnC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$\text{CH}_3(\text{CH}_2)_3\text{C}\equiv\text{CH}$	$(\text{CH}_3)_3\text{SnC}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3$	<i>e</i>	77
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	$(\text{C}_2\text{H}_5)_3\text{SnC}\equiv\text{CC}_6\text{H}_5$	<i>e</i>	77
$(\text{C}_6\text{H}_5)_3\text{SnN}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	$(\text{C}_6\text{H}_5)_3\text{SnC}\equiv\text{CC}_6\text{H}_5$	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	Cyclopentadiene	$(\text{CH}_3)_3\text{SnC}_5\text{H}_5$	<i>e</i>	77
$(\text{C}_6\text{H}_5)_3\text{SnN}(\text{CH}_3)_2$	Cyclopentadiene	$(\text{C}_6\text{H}_5)_3\text{SnC}_5\text{H}_5$	<i>e</i>	77
$(\text{C}_6\text{H}_5)_3\text{SnN}(\text{CH}_3)_2$	Indene	$(\text{C}_6\text{H}_5)_3\text{SnC}_9\text{H}_7$	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	CO_2	$(\text{CH}_3)_3\text{SnOC}(\text{O})\text{N}(\text{CH}_3)_2$	<i>f</i>	56
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	CS_2	$(\text{CH}_3)_3\text{SnSC}(\text{S})\text{N}(\text{CH}_3)_2$	<i>f</i>	56

$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{NCO}$	$ \begin{array}{c} (\text{CH}_3)_3\text{Sn} \\ \diagup \\ \text{H}_5\text{C}_6 \text{---} \text{N} \text{---} \text{CN}(\text{CH}_3)_2 \\ \quad \quad \quad \parallel \\ \quad \quad \quad \text{O} \end{array} $	<i>f</i>	56
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{NCS}$	$ \begin{array}{c} (\text{CH}_3)_3\text{Sn} \\ \diagup \\ \text{H}_5\text{C}_6 \text{---} \text{N} \text{---} \text{CN}(\text{CH}_3)_2 \\ \quad \quad \quad \parallel \\ \quad \quad \quad \text{S} \end{array} $	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{C}_2\text{H}_5)_2$	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{NCNC}_6\text{H}_4\text{CH}_3$ - <i>p</i>	$ \begin{array}{c} (\text{CH}_3)_3\text{Sn} \\ \diagup \\ p\text{-CH}_3\text{C}_6\text{H}_4 \text{---} \text{N} \text{---} \text{CN}(\text{C}_2\text{H}_5)_2 \\ \quad \quad \quad \parallel \\ \quad \quad \quad \text{NC}_6\text{H}_4\text{CH}_3\text{-}p \end{array} $	<i>e</i>	77
$(\text{CH}_3)_3\text{SnN}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{CN}$	$ (\text{CH}_3)_3\text{SnN}=\text{C} \begin{array}{l} \diagup \text{C}_6\text{H}_5 \\ \diagdown \text{N}(\text{CH}_3)_2 \end{array} $	<i>e</i>	77
$[(\text{CH}_3)_3\text{Sn}]_3\text{N}$	CH_3Li	$ \left\{ \begin{array}{l} [(\text{CH}_3)_3\text{Sn}]_2\text{NLi} \\ (\text{CH}_3)_3\text{SnNLi}_2 \end{array} \right. $	—	79

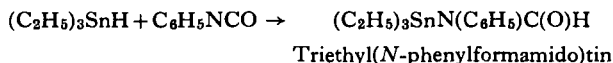
^a Probably partially polymeric.^b Isolation not successful.^c No reaction.^d Poor yield.^e Nearly quant. yield.^f Good yield (> 65%).

catalytic influence of organotin compounds on the formation of polyurethanes from diols and diisocyanates is explained.

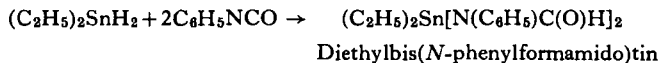
In a second paper further addition reactions of organotin alkoxides and some bis(trialkyltin) oxides are reported (95). Some of these lead to the formation of compounds with tin–nitrogen bonds, viz.



Noltes and Janssen (93, 94) have prepared a number of formamide derivatives by the addition of organotin hydrides to organic isocyanates. Triethyltin hydride, for example, reacts at room temperature with an equimolecular amount of phenyl isocyanate to give triethyl(*N*-phenylformamido)tin.

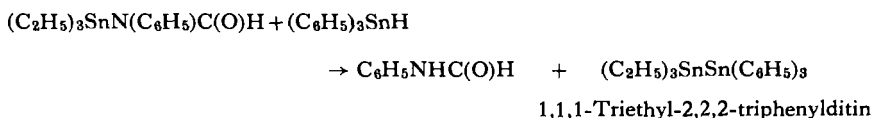


The reaction was also carried out with functionally substituted phenyl isocyanates and with *p*-phenylene diisocyanate. The reaction of diethyltin dihydride with phenyl isocyanate affords a compound with two phenylformamido groups attached to one tin atom.



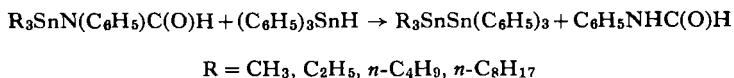
Aliphatic isocyanates, like *n*-hexyl isocyanate, react in the same manner (96). The structure of the addition products was determined by IR, UV, and NMR techniques.

The *N*-phenylformamido group in these compounds is easily cleaved by hydrolysis, *N*-phenylformamide and an organotin hydroxide being formed. The tin–nitrogen bond is also broken by triphenyltin hydride. The products are *N*-phenylformamide and a compound containing a tin–tin bond, e.g., in the case of triethyl(*N*-phenylformamido)tin, 1,1,1-triethyl-2,2,2-triphenylditin.

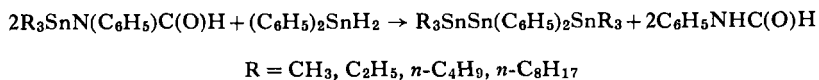


It is clear that if organic isocyanates are treated with excess of triphenyltin hydride, *N*-substituted formamides and hexaphenylditin are the only reaction products [cf. (97)].

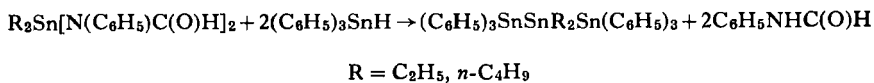
The hydrogenolysis reactions of (*N*-phenylformamido)tin compounds are not only suited to the preparation of ditin compounds, but also to the synthesis of a wide variety of compounds containing more than one tin–tin bond. Very recently Creemers *et al.* (98) published the first results of work in this area.



Two different types of mixed tritin compounds result from the reactions

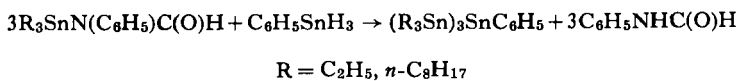


and

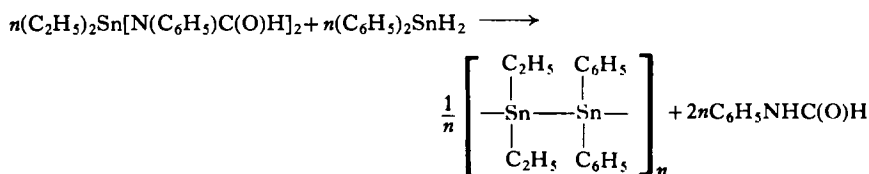


A fully arylated compound, viz. octaphenyltritin, was also prepared by this method.

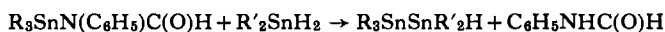
Tris(trialkylstannyl)phenyltin derivatives—tetratin compounds with a branched structure—were obtained thus:



The synthesis of a polymeric product consisting of alternate diethyl- and diphenyltin groups was realized by the reaction

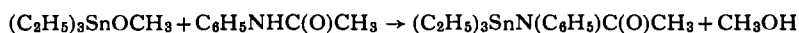


The scope of this synthetic method was considerably enlarged when it was found (99) that 1 mole of a mono(*N*-phenylformamido)tin compound reacts with 1 mole of a dialkyl- or diaryltin dihydride to give an organoditin monohydride.



These ditin monohydrides have proven to be capable of many interesting transformations.

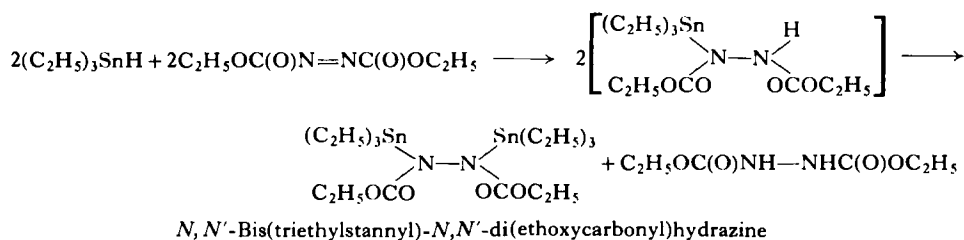
Noltes (96) recently reported the synthesis of a number of *N*-trialkyltin-substituted acylamides and carbamates by the reaction of trialkyltin alkoxides with the corresponding NH derivatives. At elevated temperatures (150°–160° C) such reactions proceed in excellent yields (67–90%). The formation of *N*-triethylstannylacetanilide is given as an example.



The products obtained from the reaction between triethyltin methoxide and *N*-hexyl- or *N*-phenylformamide were found to be identical with those obtained previously by addition of triethyltin hydride to the corresponding isocyanates (93, 94). The organotin-substituted carbamates obtained by the amidolysis reaction and those obtained by the addition of triethyltin methoxide to the corresponding isocyanate are, likewise, identical.

It may be remarked that the reaction of triethyltin methoxide with the corresponding thioacylamides or thiocarbamates affords products containing a tin–sulfur rather than a tin–nitrogen bond.

Another addition reaction important in this connection is that between triethyltin hydride and diethyl azodicarboxylate (84). Equimolecular amounts of these reactants in hexane solution spontaneously give on the one hand the reduction product diethyl hydrazinedicarboxylate and on the other hand a compound containing two triethyltin groups. It is assumed that the primary addition product very readily disproportionates.



As in the *N*-phenylformamido compounds the tin–nitrogen bond in this hydrazine derivative is readily hydrolyzed by water and hydrogenolyzed by triphenyltin hydride.

The organotin-substituted amides and related compounds are listed in Table IX.

TABLE IX
ORGANOTIN-SUBSTITUTED AMIDES AND RELATED COMPOUNDS

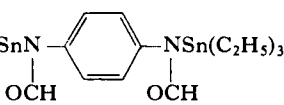
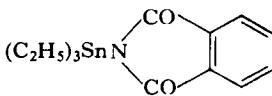
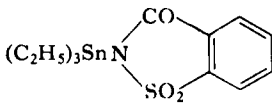
Compound	M.p. (°C)	B.p. (°C/mm)	References
<i>Substituted amides</i>			
$(\text{C}_2\text{H}_5)_3\text{SnN}(n\text{-C}_6\text{H}_{13})\text{C(O)H}$	—	105°–106°/0.1 ^a	93, 94
	—	105°–109°/0.3 ^b	96
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{C}_6\text{H}_5)\text{C(O)H}$	50°–53°	171°–172°/13	93, 94
	56°–58°	110°/0.3	96
$(n\text{-C}_4\text{H}_9)_3\text{SnN}(\text{C}_6\text{H}_5)\text{C(O)H}$	64°	170°/0.1	94
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{C}_6\text{H}_4\text{Cl-}p)\text{C(O)H}$	77°–79°	120°–122°/0.1	94
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{C(O)H}$	116°–119°	—	94
$(\text{C}_2\text{H}_5)_2\text{Sn}[\text{N}(\text{C}_6\text{H}_5)\text{C(O)H}]_2$	Cryst.	—	94
	191°–195°	—	94
$(\text{C}_2\text{H}_5)_3\text{SnN}(\text{C}_6\text{H}_5)\text{C(O)CH}_3$	46°–48°	111°–112°/0.15	96
<i>Substituted imides</i>			
	71°–73°	—	90, 91
	113.5°–114°	—	91

TABLE IX—continued

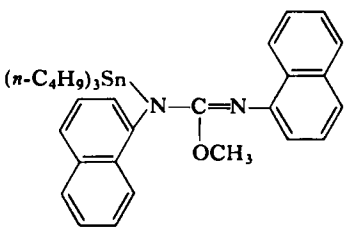
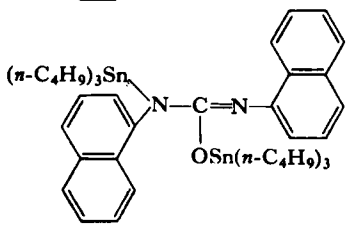
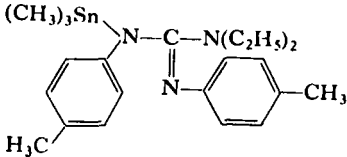
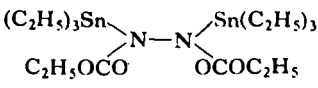
Compound	M.p. (°C)	B.p. (°C/mm)	References
<i>Sulfonamides</i>			
$(C_2H_5)_3SnNH SO_2CH_3$	38°	—	90, 91
$(n-C_4H_9)_2Sn(NH SO_2C_6H_{13})_2$	—	—	89
$(n-C_4H_9)_2Sn(NH SO_2C_6H_5)_2$	135°–137°	—	89
$(n-C_4H_9)_2Sn[N(n-C_4H_9)SO_2C_6H_5]_2$	—	—	89
$(C_2H_5)_3SnNH SO_2C_6H_4CH_3-p$	69.5°–71°	—	90, 91
$(n-C_4H_9)_2Sn(NH SO_2C_6H_4CH_3-p)_2$	—	—	89
$(n-C_4H_9)_3SnN(C_2H_5)SO_2C_6H_4CH_3-p$	—	200°/1.5	89
<i>Carbamic acid and thiocarbamic acid derivatives</i>			
$(C_2H_5)_3SnN(n-C_4H_9)C(O)OC_2H_5$	—	57.5°/0.01	92
$(C_2H_5)_3SnN(n-C_6H_{13})C(O)OCH_3$	—	92°–93°/0.2°	96
$(C_2H_5)_3SnN(C_6H_5)C(O)OCH_3$	—	105°–108°/0.4°	96
$(n-C_4H_9)_3SnN(C_6H_5)C(O)OCH_3$	—	99°–100°/0.01	92
$(C_2H_5)_3SnN(1-C_{10}H_7)C(O)OC_2H_5$	86°–93°	108°/0.05	92
$(n-C_4H_9)_3SnN(1-C_{10}H_7)C(O)OCH_3$	—	120°/0.01	92
$(n-C_3H_7)_3SnN(C_6H_5)C(O)OSn(n-C_3H_7)_3$	—	—	95
$(n-C_4H_9)_3SnN(C_6H_5)C(S)OCH_3$	—	68°/0.02	92
<i>An imido ester</i>			
$(n-C_4H_9)_3SnN=C-CCl_3$ $ $ OCH_3	—	—	95
<i>Urea and thiourea derivatives</i>			
$(C_2H_5)_3SnNHC(O)NH_2$	—	—	50
$(CH_3)_3SnN(C_6H_5)C(O)N(CH_3)_2$	—	103°/0.5	56
$(CH_3)_3SnN(C_6H_5)C(S)N(CH_3)_2$	—	Liquid	77
<i>Isourea derivatives</i>			
	—	—	95
	—	—	95

TABLE IX—continued

Compound	M.p. (°C)	B.p. (°C/mm)	References
<i>Guanidine, amidine, and carbodiimide derivatives</i>			
	—	168°/0.1	77
$(\text{CH}_3)_3\text{SnN}=\text{C}(\text{C}_6\text{H}_5)\text{N}(\text{CH}_3)_2$	—	79°/0.2	77
$(\text{C}_6\text{H}_5)_3\text{SnN}=\text{C}=\text{NSn}(\text{C}_6\text{H}_5)_3$	99°–100.5°	—	100
<i>Hydrazine derivatives</i>			
	—	156°/0.1 ^e	84

^a $n_D^{20} = 1.4910$.^b $n_D^{20} = 1.4918$.^c $n_D^{20} = 1.4784$.^d $n_D^{20} = 1.5388$.^e $n_D^{20} = 1.4998$.

E. Substituted Heterocycles

1. Introduction

Only a relatively few organotin-substituted heterocycles are known as compared with the large number of organotin-substituted aliphatic and aromatic compounds. Those described in this section, i.e. compounds with an organotin group joined to a nitrogen atom which is contained in a ring, were unknown until 1962.⁸ In that year Luijten, Janssen, and Van der Kerk (3, 42) reported the preparation and properties of a number of these compounds.

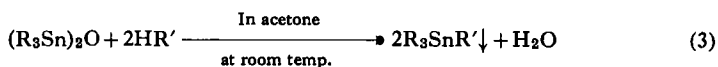
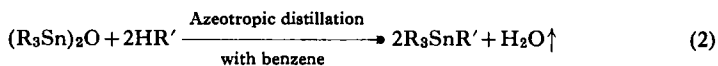
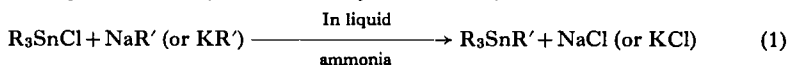
From this study it appeared that two types must be distinguished, one resembling the substituted amines and sensitive toward water, the other

⁸ The results reported in this section represent a summary of investigations carried out at the authors' institute.

unexpectedly stable toward this reagent. The sensitive compounds are triorganotin derivatives of pyrrole, pyrazole, and benzpyrazole and some compounds in which two heterocyclic residues are bound to tin. The stable ones are triorganotin-substituted imidazole, 1,2,3- and 1,2,4-triazole, and condensed imidazoles and triazoles. The occurrence in the stable compounds of two nitrogen atoms in a 1,3-position led to the supposition that the stability might be due to the complexing ability of the second nitrogen atom with formation of a coordination polymer with pentacoordinated tin. Infrared spectroscopy and X-ray analysis have largely confirmed this prediction.

2. Preparation

Apart from a few instances (*N*-triphenylstannylpyrrole, *N*-trimethylstannylimidazole) in which a Grignard procedure was used, three major methods of preparation were employed in the synthesis of the organotin-substituted heterocycles (100). Schematically they can be represented by the following equations ($R' =$ heterocyclic radical):



Method (1) had to be applied when no organotin oxide or hydroxide, but only the halide was available, and also in the case of benzpyrazole. All trimethyltin derivatives were prepared by this route, because at the time no suitable method was known for the preparation of trimethyltin hydroxide. A convenient method of preparation of this compound has recently been found (101).

Method (2) proved to be the most suitable for preparing tributyltin derivatives which generally have low melting points and are too soluble in acetone to permit their preparation by Method (3).

The triphenyltin derivatives, *N*-tripropylstannylimidazole and *N*-tributylstannylbenzimidazole are very easily prepared by Method (3) which consists of a simple mixing of acetonic solutions of the starting materials and filtering off the precipitate formed.

Data on the organotin-substituted heterocycles are collected in Table X.

TABLE X
ORGANOTIN-SUBSTITUTED HETEROCYCLES














Compound	M.p. (°C)	B.p. (°C/mm)	n_D^{20}	References
$(\text{CH}_3)_3\text{SnN}$ 	—	101.5°–102°/17	1.5302	100
$(n\text{-C}_4\text{H}_9)_3\text{SnN}$ 	—	139°–141°/0.62	1.4952	100
$(\text{C}_6\text{H}_5)_3\text{SnN}$ 	203.2°–204°	—	—	100
$(n\text{-C}_4\text{H}_9)_3\text{SnN}$ 	—	98°–102°/0.04	1.4995	100
$(\text{CH}_3)_3\text{SnN}$ 	234°–236°	—	—	3, 42
$(n\text{-C}_3\text{H}_7)_3\text{SnN}$ 	235°–238° (dec)	—	—	100
$(n\text{-C}_4\text{H}_9)_3\text{SnN}$ 	152°–154°	—	—	3, 42
$(n\text{-C}_4\text{H}_9)_3\text{SnN}$ 	149°–150°	—	—	100
$(\text{C}_6\text{H}_5)_3\text{SnN}$ 	65°–67°	—	—	3, 42
$(\text{C}_6\text{H}_5)_3\text{SnN}$ 	64°–64.5°	—	—	100
$(\text{C}_6\text{H}_5)_3\text{SnN}$ 	304°–305.5°	—	—	42
$(\text{C}_6\text{H}_5)_3\text{SnN=N}$ 	310°–311°	—	—	100
$(\text{CH}_3)_3\text{SnN=N}$ 	311°–313° (dec)	—	—	100

TABLE X—continued


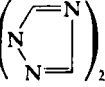
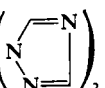

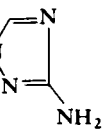
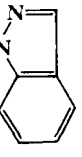
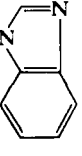
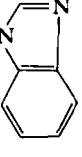
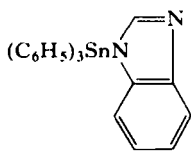
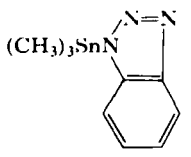
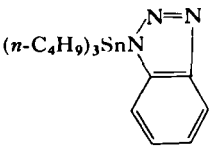
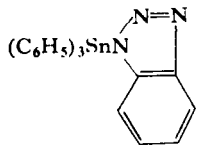
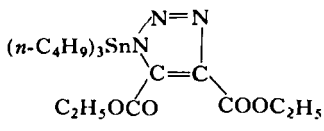
Compound	M.p. (°C)	B.p. (°C/mm)	n_D^{20}	References
$(n\text{-C}_4\text{H}_9)_3\text{SnN}$ 	277°–278°	—	—	3
	277°–278° (dec)	—	—	42, 100
$(\text{C}_2\text{H}_5)_2\text{Sn}$  ₂	66°–71°	—	—	3, 42, 100
	Infusible	—	—	100
$(n\text{-C}_4\text{H}_9)_2\text{Sn}$  ₂	Dec at 240°	—	—	100
	294°–295.5°	—	—	42, 100
$(\text{C}_6\text{H}_5)_3\text{SnN}$ 	196°–197°	—	—	100
$(\text{C}_2\text{H}_5)_3\text{SnN}$ 	—	124°–128°/0.002	1.5376	100
$(n\text{-C}_4\text{H}_9)_3\text{SnN}$ 	Subl. > 200°	—	—	3, 42, 100
$(\text{CH}_3)_3\text{SnN}$ 	137.5°–139°	—	—	3, 42, 100
$(n\text{-C}_4\text{H}_9)_3\text{SnN}$ 	Dec at 298°	—	—	42, 100

TABLE X—continued

Compound	M.p. (°C)	B.p. (°C/mm)	n_D^{20}	References
	221.5°–223°	—	—	3
	221.5°–223° (dec)	—	—	42, 100
	78°–88°	—	—	3, 42, 100
	270.5°–272°	—	—	42, 100
	64.5°–67°	—	—	102

3. Properties

The organotin-substituted heterocycles, with the exception of the trialkylstannyldipyrroles and -pyrazoles, are well-crystallized solids, the tributyltin compounds having low melting points.

As already stated in Section IIIA, trialkyl- and triaryltin derivatives of pyrrole, pyrazole, and benzpyrazole are decomposed by water. The same holds for a few compounds in which two 1,2,4-triazolyl groups are bound to tin. In

sharp contrast is the high stability of triorganotin-substituted imidazole, 1,2,3- and 1,2,4-triazole, benzimidazole, and 1,2,3-benzotriazole. This is perhaps best illustrated by the fact that *N*-trimethylstannylimidazole can be recrystallized from boiling water. The inertness toward water was sometimes used to advantage to purify crude reaction products by washing with water to remove water-soluble impurities like sodium chloride, imidazole, etc.

A peculiar property observed during the preparation of some tributyltin derivatives was the high viscosity of benzene solutions of these compounds.

4. Structural Considerations

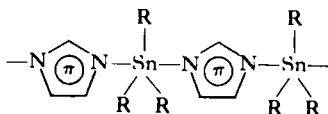
Physicochemical examination of the above compounds began with a closer study of the action of water (42). From the shape of the titration curves obtained by potentiometric titration of solutions of *N*-trimethylstannylimidazole and *N*-trimethylstannyl-1,2,4-triazole, it was concluded that the compounds were completely hydrolyzed in aqueous solution. Consequently, the stability toward hydrolysis mentioned earlier has to be understood in terms of a stabilization of the crystalline state.

All stable derivatives contain a radical with at least two nitrogen atoms, occupying 1,3-positions relative to each other. Nitrogen in any other position is not able to stabilize the organotin compound (pyrazole) or to destabilize it (1,2,3-benzotriazole). Thus the crystal stabilization is probably due to the coordinating action of the second nitrogen atom. Since intramolecular coordination is sterically impossible, some kind of association has to be involved.

Further information was obtained from a study of the infrared spectra in the potassium bromide region. Trimethyltin compounds normally give rise to two Sn—C vibrations at about 500 and 550 cm^{-1} , belonging to the symmetrical and the asymmetrical Sn—C stretching vibrations of tetrahedral molecules, respectively (103, 104). Only one band (near 550 cm^{-1}) is expected, however, for the planar $(\text{CH}_3)_3\text{Sn}$ configuration. Thus absence of the 500 cm^{-1} band in trimethyltin fluoride and acylates (103) has been used as evidence for the occurrence of planar $(\text{CH}_3)_3\text{Sn}^+$ ions in these compounds.

N-Trimethylstannylimidazole and -triazole showed only the 550 cm^{-1} band, whereas *N*-trimethylstannylpyrrole clearly showed both bands. Consequently, in the former compounds a planar configuration of the methyl groups around the tin atom has to be assumed.

Instead of the ionic structure of Okawara *et al.*, Luijten *et al.* (42) proposed a structure with pentacoordinated tin, in which two axial positions are occupied by the nitrogen atoms of imidazole units. Schematically this may be represented as follows:



The validity of this hypothesis has been checked by X-ray analysis.

Next, the possible existence of coordination polymers in solution was investigated (43). The viscosity of solutions of *N*-tributylstannylimidazole and *N*-tributylstannyl-1,2,4-triazole in toluene was found to be highly dependent on concentration. No viscosity increase was found, however, for *N*-tributylstannylpyrrole and -pyrazole. Obviously, a coordination polymer is present in not too dilute solutions ($> 0.5\%$ or about $0.01\text{ }M$) of the former organotin derivatives (Fig. 2).

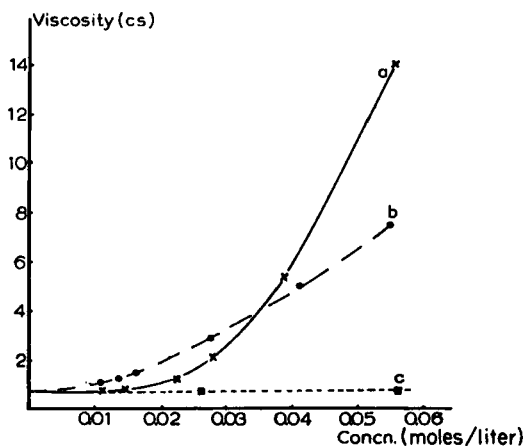


FIG. 2. The viscosity of solutions of organotin derivatives in toluene at 20.0°C : (a) *N*-tributylstannylimidazole; (b) *N*-tributylstannyl-1,2,4-triazole; (c) *N*-tributylstannylpyrrole and *N*-tributylstannylpyrazole.

From experiments with competing complexing agents Janssen *et al.* (43) came to the tentative conclusion that the unusual stability of the coordination polymers under consideration is due to additional d_{π} bonding through back-donation from the tin atoms towards the heterocyclic ligands.

IV

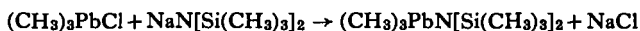
LEAD

The number of known organolead-nitrogen compounds is small. Nevertheless representative compounds of the several possible classes are known.

A few organolead complexes have been mentioned in the early literature. Pfeiffer *et al.* (105) found that diphenyllead dibromide, dichloride, and dinitrate crystallize from hot pyridine as $(C_6H_5)_2PbX_2 \cdot 4C_5H_5N$. These complexes are stable when kept in a pyridine atmosphere. In air pyridine is lost with the formation of white powders which probably are complexes containing only two molecules of pyridine. Diphenyllead dibromide forms a complex with two molecules of ammonia when kept in a stream of dry ammonia at room temperature. This complex again is unstable: In air ammonia is gradually given off (see also ref. 106).

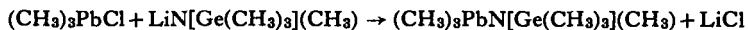
An organolead chelate complex with lead-nitrogen bonds was recently examined (64). Diphenyllead bis(8-hydroxyquinolate), like the corresponding tin compound, probably has an octahedral structure.

The first organolead-substituted amine, triethyl(*sec*-butylamino)lead was patented in 1959 as a herbicide (107). It was prepared from triethyllead chloride and sodium *sec*-butylamide in refluxing benzene. On exposure to air it slowly hydrolyzes. The other two known substituted amines in addition to lead contain silicon and germanium, respectively. Trimethylplumbyl-bis(trimethylsilyl)amine (36) has been prepared by the reaction



In a few papers the occurrence of π bonding between germanium, tin, or lead and nitrogen has been discussed. Scherer and Schmidt (35, 36) have compared the infrared spectra of the compounds $(CH_3)_3M^{IV}N[Si(CH_3)_3]_2$. A shift was observed of the asymmetric Si—N vibrations to higher frequencies in the order $M^{IV} = Si, Ge, Sn, \text{ and } Pb$. This was interpreted as a consequence of decreasing π bonding in the M^{IV} —N bonds in this sequence. From nuclear magnetic resonance spectra the same conclusion was drawn (36, 37). Another interesting type of compound must be mentioned in this context, viz. the Group IVB organometallic azides (108, 109, 110).

From trimethyllead chloride and lithium trimethylgermyl-methylamide the compound trimethylplumbyl-trimethylgermyl-methylamine has been prepared (29).



During the Second World War a number of triorganolead-substituted sulfonamides, phthalimides, and a sulfimide were prepared and tested as potential sternutators (111, 112, 113). The methods of preparation included the reaction of triethyl- or tripropyllead chloride with the sodium derivative of a sulfonamide, and the reaction between triethyl- or tripropyllead hydroxide and a sulfonamide. Both reactions were generally carried out in ethanol, and the product was precipitated by the addition of water. This demonstrates the hydrolytic stability of these compounds. The phthalimides and the sulfimide were prepared from the organolead hydroxides. They show the same high hydrolytic stability.

Two substituted imides, viz. *N*-triethylplumbylphthalimide and -tetrachlorophthalimide, and one substituted hydrazide, viz. *N*-triethylplumbylphthalohydrazide, have been described in the patent literature as fungicides (114, 115). The imides were prepared from triethyllead hydroxide and phthalimide, or tetrachlorophthalimide in ethanol. *N*-triethylplumbylphthalohydrazide (or *N*-triethyllead-2,3-dihydro-1,4-phthalazinedione as it is called in the patent) was obtained from the reaction between sodium hydroxide, phthalohydrazide, and triethyllead chloride in water. The crude hydrazide is purified by precipitating it in ethanolic solution with water.

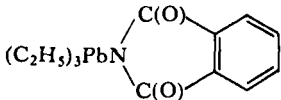
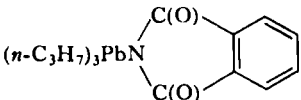
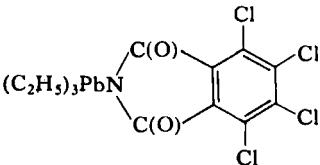
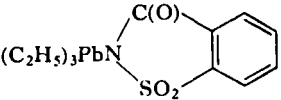
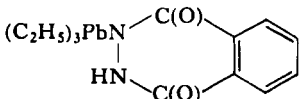
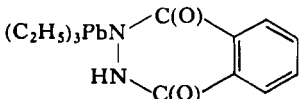
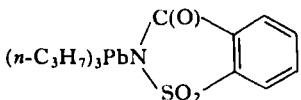
Organolead-substituted heterocycles have been prepared by Willemsens (116, 118).

The known organolead-nitrogen compounds have been summarized in Table XI.

TABLE XI
ORGANOLEAD-NITROGEN COMPOUNDS

Compound	M.p. (°C)	B.p. (°C/mm)	References
(C ₆ H ₅) ₂ PbBr ₂ · 4C ₅ H ₅ N	—	—	105
(C ₆ H ₅) ₂ PbCl ₂ · 4C ₅ H ₅ N	—	—	105
(C ₆ H ₅) ₂ Pb(NO ₃) ₂ · 4C ₅ H ₅ N	—	—	105
(C ₆ H ₅) ₂ PbBr ₂ · 2NH ₃	—	—	105
(C ₆ H ₅) ₂ Pb(oxin) ₂ ^a	—	—	64
(C ₂ H ₅) ₃ PbNHCH(CH ₃)C ₂ H ₅	—	—	107
(CH ₃) ₃ PbN[Si(CH ₃) ₃] ₂	—	85°–87°/3	36
(CH ₃) ₃ PbN[Ge(CH ₃) ₃](CH ₃)	—	49°/2	29

TABLE XI—continued

Compound	M.p. (°C)	B.p. (°C/mm)	References
	131°	—	112
	—	—	115
	—	—	112
	—	—	115
	—	—	114
	135°	—	113
	130°	—	113
(C ₂ H ₅) ₃ PbNHSO ₂ CH ₃	97°	—	113
(<i>n</i> -C ₃ H ₇) ₃ PbNHSO ₂ CH ₃	67°	—	113
(C ₂ H ₅) ₃ PbN(C ₆ H ₅)SO ₂ CH ₃	115.5°	—	113
[(C ₂ H ₅) ₃ PbN(C ₆ H ₅)SO ₂] ₂ CH ₂	(dec 180°)	—	113
(C ₂ H ₅) ₃ PbN(C ₆ H ₅)SO ₂ CH=CH ₂	116° ^b	—	113
(C ₂ H ₅) ₃ PbNHSO ₂ C ₆ H ₅	132°	—	113
(<i>n</i> -C ₃ H ₇) ₃ PbNHSO ₂ C ₆ H ₅	96°	}	113
	93.5°–94.5°		
(C ₂ H ₅) ₃ PbNHSO ₂ C ₆ H ₄ NH ₂ - <i>p</i>	171°	—	113

$(n\text{-C}_3\text{H}_7)_3\text{PbNHSO}_2\text{C}_6\text{H}_4\text{NH}_2\text{-}p$	101°	—	113
$(\text{C}_2\text{H}_5)_3\text{PbNHSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}o$	133°	—	113
$(\text{C}_2\text{H}_5)_3\text{PbNHSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	127°	—	113
$(n\text{-C}_3\text{H}_7)_3\text{PbNHSO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	100°–101°	—	113
$(\text{C}_2\text{H}_5)_3\text{PbN}(\text{C}_6\text{H}_5)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	134°	—	113
$(n\text{-C}_3\text{H}_7)_3\text{PbN}(\text{C}_6\text{H}_5)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	104°	—	113
$(\text{C}_2\text{H}_5)_3\text{PbN}(\text{C}_6\text{H}_4\text{Cl-}p)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	111.5°	—	113
$(n\text{-C}_3\text{H}_7)_3\text{PbN}(\text{C}_6\text{H}_4\text{Cl-}p)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	123°	—	113
$(\text{C}_2\text{H}_5)_3\text{PbN}(\text{C}_6\text{H}_4\text{Br-}p)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$	117°	—	113

^a oxin = 8-hydroxyquinolate.

^b When heated up slowly.

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